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Studies on the Production and Evaluation of
Selected Starch-Reinforced Rubbers

Final Report

by

Brooks Wolfe
Donald E. Wright
Frank J. Male
Robert W. Hallman

November 30, 1973

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SUMMARY

Masterbatches formed by the co-coagulation of starch xanthate mixed with rubber latex were studied on a bench scale and pilot plant scale. Based on bench scale experiments, the zinc starch xanthate/rubber masterbatches were not scaled up because extremely fine coagulation crumbs were obtained and the rubber physical properties were not satisfactory. Rapid in-line co-coagulation of the starch xanthate and rubber latex is necessary to reproducibly obtain masterbatches with satisfactory rubber properties. Coagulation parameters affecting the crumb characteristics are: final serum pH (1.5-2.0), coagulation temperature (cool), and fatty acid emulsified latexes rather than rosin acid emulsified latexes. Crude filtering studies indicated the final filter cake will contain only 25% solids with 75% water. Dewatering presses are not suitable for these starch masterbatches.

The University of Akron discovery that extrusion processing of slightly wet (10%) masterbatches enhances physical properties was confirmed. The rubber-in-starch phase system obtained during coagulation must be inverted to a dispersion of fine starch particles in a continuous rubber phase to obtain rubbery properties. The mixing that occurs during compounding is not sufficient to invert the phases. Electron microscopy can be used to study the starch dispersion and particle size in the masterbatches. The extrusion process was successfully scaled-up from the Brabender laboratory extruder to the pilot plant scale V.D. Anderson Expander Dryer. The physical properties are not very sensitive to the extrusion conditions.

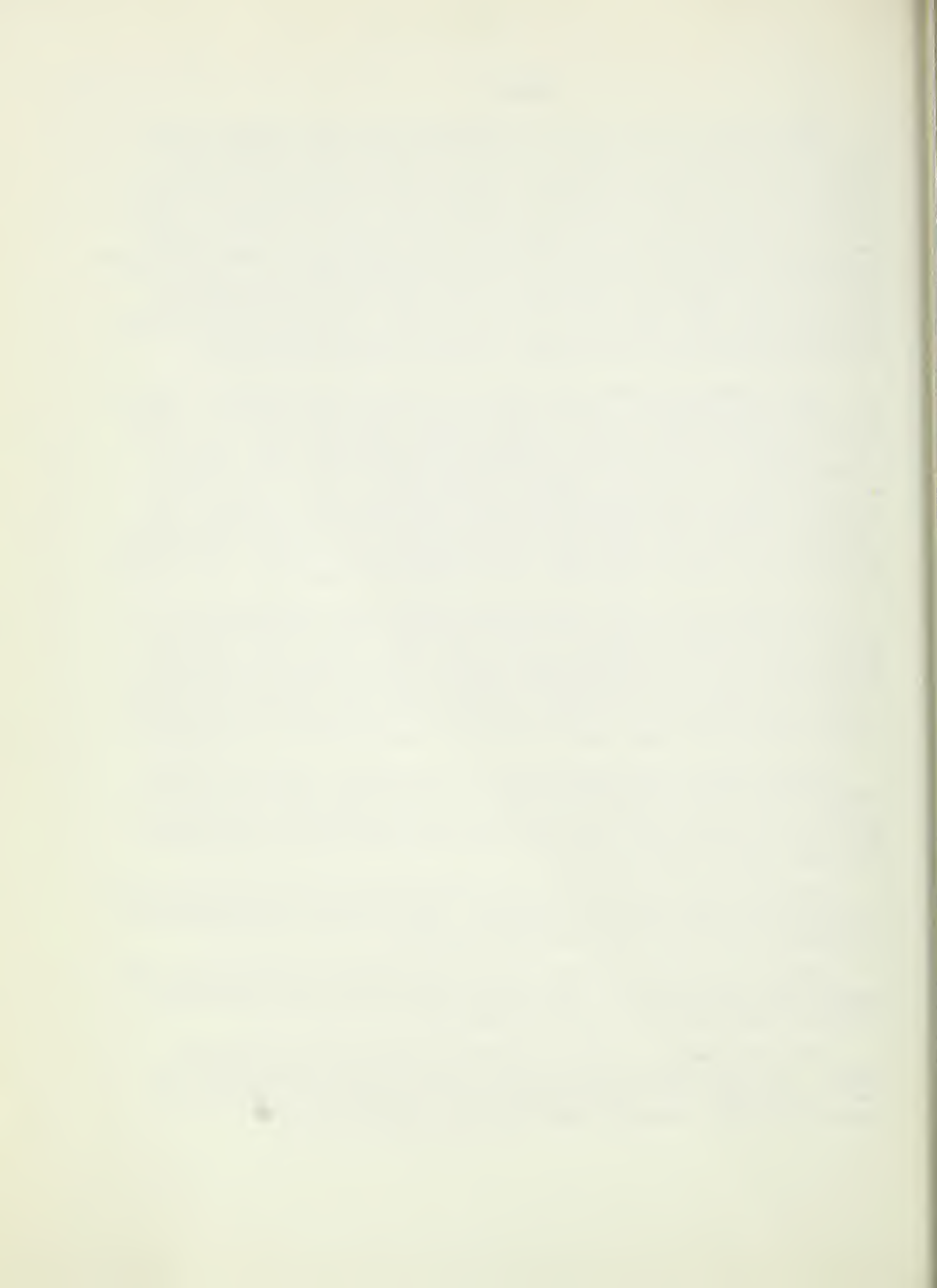
The estimated cost of incorporating starch in SBR, including raw material usage, extra direct labor for the xanthation process, extra indirect labor such as laboratory technicians, extra drying costs, capital depreciation on a \$1.6 MM investment, and a 12% BFIT return on investment, is 11.0 cents per pound of starch. All the extra costs involved in making a starch masterbatch over and above the costs for producing the black pigmented rubber are charged against the starch rather than the masterbatch.

Starch xanthate masterbatches can be successfully cured with typical sulfur accelerator cure systems. The nitrile/starch masterbatches in general yield higher physical properties than the SBR/starch masterbatches. Also, their excellent oil resistance gives them the ability to be used to meet many product specifications.

The SBR/starch masterbatches can be blended with SBR black masterbatches to yield fairly high physical properties. These stocks are applicable for retreading tires or for various molded products.

Several tires were retreaded using a 50/50 blend of SBR/starch and SBR carbon black masterbatches. Some molded products were cured successfully using this same stock and a nitrile/starch MB.

The nitrite/starch stock was developed to meet ASTM specification 2BG615. The only property that failed to meet the specification was the water resistance. Poor water resistance is a weakness of starch polymer masterbatches that probably would limit their potential use.



DISCUSSION

PROCESS DEVELOPMENT

Coagulation Process Development

All the published work involving the co-coagulation of starch xanthates with rubber latexes preceeding the BFG work used batch processes. The University of Akron extensively studied the agitation requirements for batch coagulations. The viscosity variations that occur during a batch coagulation cause many problems in designing agitation for the coagulator. Continuous coagulation studies were recommended by the University of Akron. A continuous coagulation process offers a number of advantages over a batch process:

- (1) The viscosity changes that occur during coagulation are localized to the incoming stream only, rather than an entire tank.
- (2) The coagulation conditions can be controlled better since the time of coagulation is reduced and occurs in a constant environment. Better control may give an improved product.
- (3) A continuous process is generally more economical on a production scale than a batch process with its intermittent flows and time delays.
- (4) Since the bulk viscosity is reduced, the gas (nitrogen oxide) evolution is facilitated. Also, the gas evolution will be constant rather than being released in a large volume at one point during a coagulation as in a batch process.

With these potential advantages in mind, bench scale experiments were conducted in which a continuous coagulation process was simulated. The following procedure was used:

SBR 1509 latex was pre-blended with a 10% Hoosier Pearl corn starch xanthate solution (0.06-0.07 DS) and sufficient sodium nitrite to cross-link the starch. The general procedure was to prepare enough coagulation serum for good agitation in the coagulator. The coagulation serum consisted of water and sufficient sulfuric acid to reduce the pH to the desired level. The latex/SX preblend (Xantex) was slowly poured into the coagulation serum under agitation. The coagulation serum was maintained at the desired pH by addition of a 2% sulfuric acid solution. Because the rates were controlled manually the pH drifted as much as ± 0.5 pH units. Coagulation pH and temperature were evaluated. The best coagulation pH was found to be 4.0-5.0. As the coagulation pH was reduced, the crumb size became smaller. Higher coagulation pH's gave incomplete coagulation of the rubber and/or starch. The continuous coagulation gives a more uniform particle size than batch coagulations, probably because the entire amount is coagulated under the same conditions. Batch coagulations, particularly when a viscous stage is involved, tend to have localized high concentrations of acid (low pH) which give smaller crumbs.

The quality of the continuous coagulation product is nearly equivalent to the batch coagulated control (Table I). Except when batch coagulations are specifically labelled, all further bench scale coagulations were the semi-continuous (simulated continuous) process.



TABLE I

EVALUATION OF 45 PHR STARCH XANTHIDE/SBR MASTERBATCHES COAGULATED UNDER VARYING CONDITIONS

<u>Sample</u>	<u>5-P3-A</u>	<u>6-P3-B</u>	<u>6-P3-C</u>	<u>7-P3-CA</u>
Latex	1509	1509	1509	1509
Coagulation	Batch	Batch	Semi-cont.*	Semi-cont.*
Description	Acid	Acid Heat	Acid Heat No Aggl.	Acid Heat Aggl.
Final Coag. pH	2.3	4.2	1.6	4.3
Wash pH	2.5	6.6	2.3	6.7
<u>Rheometer</u>				
Min. Visc.	4.5	4	3.5	4.5
Scorch, Mins.	11.5	6	15	6.5
<u>50% T Max.</u>				
Cure Time, mins.	21	12	27	12
M ₂₀₀ , psi	1050	750	650	700
Tensile, psi	1400	1350	1300	1350
Elongation, %	310	420	310	400
Durometer A	64	66	58	63
<u>90% T Max.</u>				
Cure Time, mins.	33	18	45	19
M ₂₀₀ , psi	1100	800	750	700
Tensile, psi	1450	1300	1400	1300
Elongation, %	270	360	300	370
Durometer A	66	65	59	64

Starch: Hoosier Pearl Corn Starch

Starch Xanthate: 0.06-0.07 DS

Semi-Continuous: Latex/SX/NaNO₂ Blend add to a 2% H₂SO₄ sol'n. containing enough acid to coagulate the entire blend.

All samples "extrusion dried" with a minimum of 3 passes; barrel temp. 125, 125, 150°C.

SBR 1509: nominal 23.5% Bound Styrene
nominal 30 ML Viscosity
Mixed Acid Emulsifier



Zinc Starch Xanthate

Zinc sulfate/acid coagulated starch xanthate/SBR masterbatches are said to have two advantages: (1) clear coagulation serum and (2) little or no odor during extrusion drying. The zinc sulfate coagulated masterbatches, however, have a very fine coagulation crumb. Thus, process development work was started to improve the coagulation crumb size. The batch coagulation indeed gave a fine crumb which is very difficult to filter. Generally, the processes which simulated continuous coagulations gave a finer, more fragile crumb but, also the cleanest serum. As the zinc sulfate level decreased the serum became more cloudy indicating starch losses. Substitution of magnesium sulfate (Epsom salt) for zinc sulfate gave a poor coagulation with high starch losses. It is felt that processes which rely on zinc sulfate for the actual coagulation may be difficult to successfully scale-up on a continuous basis. The addition of the Xantex to a zinc sulfate bath necessarily means that some zinc sulfate will be discharged in the serum. Since the SX solution and latex each bring in fresh water, some serum must be discharged as effluent. Economic and pollution considerations make such a discharge undesirable. Thus, the blending of the zinc sulfate solution with the SX or SX/latex blend seems best. Carrying this reasoning a little further indicates the zinc sulfate should be blended with the SX solution before the latex is added. In an SX/latex blend the zinc has two reaction sites -- the starch xanthate and the latex emulsifier (organic acid soap). The reaction with the starch xanthate is preferred since this cross-links the starch. The reaction with the organic acid soap will destabilize or coagulate the latex but other coagulants, such as sulfuric acid, can accomplish this. Furthermore, a preformed zinc starch xanthate may tend to give a starch in rubber rather than a rubber in starch composition. This may be desirable from both a process standpoint and a property standpoint.

Based on these factors and the better coagulation crumbs, the process involving pre-reaction of the starch xanthate with the zinc sulfate was chosen for further study. Seven masterbatches were prepared for physical testing. In this series it was found that cold coagulations give a better coagulation crumb than hot coagulations. This series also indicated better crumb size with lower starch levels. When the zinc level was decreased, the coagulation pH had to be lowered and, as before, the serum became cloudy. Resorcinol/formaldehyde modification seemed to improve the serum clarity at the lower zinc level. One sample was prepared without extrusion drying to determine if this coagulation procedure gives a good starch in rubber dispersion. These masterbatches along with a batch coagulated control (23-P-11-1) were tested for physical properties. None of the samples, including the control, gave satisfactory physical properties (Table II).



TABLE II

Evaluation of Experimental SBR 1509/Zinc Starch Xanthate Masterbatches

Compound No.	A9A	B	C	D	E	F	G	H
Sample No.	23P11-1	23P12-1	29P12-2	30P12-3	30P12-4	31P12-5	31P12-6	32P12-7
Coagulation	Batch	Semi-Continuous						
ZnSO ₄ as phr	4.0	4.0	4.0	1.0	1.0	1.0	1.0	4.0
Starch, phr	45	45	30	45	30	45	30	45
				RF	RF			No Extrd. Drying
Recipe								
Masterbatch	149	149	134	146	131	149	134	149
Zinc Oxide	1	1		4	4	1	1	5
Stearic Acid	1.5)							
Altax	3.0)							
AgeRite Powder	1.25)							
Sulfur	2.0)							
Physical Testing								
Cure Time @ 293°F	30'	60'	60'	30'	30'	30'	30'	60'
200% Modulus, psi	500	350	300	600	400	250	250	400
300% Modulus, psi	600	400	350	900	550	--	--	--
Tensile, psi	600	400	350	900	550	250	250	400
Elongation, %	400	300	300	300	300	200	200	200
Durometer A	62	62	53	62	56	60	54	67

Batch Coagulation: Latex & SX Blended, Acid added, ZnSO₄ Sol'n added to coagulate, drain serum, air dry, wet with 15% water, extruder dry.

Semi-Continuous Coag.: SX & ZnSO₄ Sol'n mixed, latex added, blend poured slowly into pH 6-7 serum, maintain coagulation pH with add'n of 2% H₂SO₄, drain serum, air dry, wet with 15% water, extruder dry.

Starch: Hoosier Pearl Corn Starch

Xanthate: 0.07-0.08 D.S. (estimated)

RF: 0.03 moles resorcinol/mole starch, 0.1 moles formaldehyde/mole starch



The BFG data indicated that zinc sulfate coagulated starch xanthate/SBR 1503 masterbatches have poor physical properties. To cross-check between laboratories, the USDA Peoria laboratory prepared two zinc starch xanthate/SBR masterbatches for BFG evaluation. BFG prepared similar masterbatches using both batch and semi-continuous methods. The batch coagulations had very fine (small) crumb sizes. A buchner funnel and filter paper had to be used to drain the serum from the crumb. The semi-continuous process involves blending SX, zinc sulfate solution, latex + NEPA antioxidant in that order; and then continuously adding this blend to a pH 6-7 coagulation serum under agitation. Although the crumb was small, the serum could be drained from the crumb using cheesecloth.

The physical testing evaluation of these masterbatches is shown in Table VI. All the zinc starch xanthate/SBR masterbatches, including the sample from the USDA Peoria laboratory, showed poor physical properties, particularly tensile strength. All the zinc starch xanthate modified with resorcinol/formaldehyde/SBR masterbatches showed acceptable physical properties. There are no significant differences either between the coagulation processes or the different laboratories.

Zinc sulfate coagulated starch xanthate/SBR masterbatches were not recommended for scale-up. While a clear coagulation serum can be obtained, the crumb, even under the best conditions, is difficult to handle. The need for resorcinol/formaldehyde modification to obtain acceptable physical properties eliminates the color advantage for the zinc sulfate coagulated masterbatches.



TABLE III
EVALUATION OF ZINC STARCH XANTHATE/SBR MASTERBATCHES

Sample No.	49P19-1	49P19-2	50P19-3	50P19-4	9290:95	9290:96
Starch, phr	30	30	30	30	30	30
Zn as phr ZnO	4	4	4	4	4	4
RF, molar	--	--	.1	.1	--	.1
Coagulation	Batch	Cont.	Batch	Cont.	Batch	Batch
Drying	Extruder	Extruder	Extruder	Extruder		
Prepared at	IDC	IDC	IDC	IDC	USDA	USDA
SBR	1503	1503	1503	1503	1511	1511
<u>Compound Recipe</u>						
Masterbatch	134	134	134	134	134	134
ZnO	1	1	1	1	1	1
Stearic Acid	1.5	1.5	1.5	1.5	1.5	1.5
Altax	3	3	3	3	3	3
PBNA	1.25	1.25	1.25	1.25	1.25	1.25
Sulfur	2	2	2	2	2	2
<u>Rheometer</u>						
Min.Torque,in-lbs.	3.0	2.9	3.2	3.1	2.5	3.5
Max.Torque,in-lbs.	69	45	66	66	31	34
t _{A2} , min.	5.8	25	7.2	8.4	28	27
t ₉₀ , min.	27	60	33	39	60	60+
<u>Physical Properties</u>						
300% Modulus, psi	300	250	850	800	200	600
Tensile, psi	350	300	1800	1400	250	1750
Elongation, %	370	380	530	490	460	610
Hardness, Duro A	58	54	59	58	49	52



Antioxidant Study

Starch xanthide/rubber masterbatches are made by coagulating a blend of rubber latex and starch xanthate containing sodium nitrite (NaNO_2) with acid. The sodium nitrite, a strong oxidizing agent under acidic conditions, is needed to cross-link the starch. In the original USDA procedure for bench scale work, the rubber antioxidant or stabilizer was added on the mill after drying to avoid the oxidizing coagulation environment. While this is satisfactory for bench scale work, it is not satisfactory for a commercial scale. The easiest method of incorporating the stabilizer is adding it as an emulsion to the latex before coagulation. This experiment was made to determine if this is feasible with any of the commonly used non-staining SBR stabilizers.

Samples of SBR 1509 containing no starch were prepared with several commonly used SBR stabilizers. The stabilizers were emulsified and added to the SBR latex. The latex was then split into two sections. The first section was salt-acid coagulated, washed once, and air dried at 180°F . The second section was treated with 1.1 phr sodium nitrite (NaNO_2) which is about 60% of the level used for a 45 phr starch xanthide/rubber masterbatch. Normally, a 25% excess sodium nitrite is used in a starch xanthide/SBR masterbatch coagulation. The second section was coagulated under the same conditions as the first section. While there were some subtle color differences in some of the samples, no drastic color differences were obtained at any stage.

The dried samples were aged in a 105°C air oven for 0 to 14 days. Mooney viscosity was determined for each sample for each aging period. The data are shown in Table IV.

Figure 1 shows the aging differences between the oxidized and nonoxidized samples without stabilizer and with AgeRite Stalite. The aging of a 5 phr starch xanthate/rubber masterbatch (coagulated with NaNO_2) present is also shown. The presence of the NaNO_2 drastically reduced the effectiveness of Stalite. However, the presence of some starch xanthate significantly reduced the effect of NaNO_2 . This indicates that the most severe conditions were chosen for this evaluation.

The differences between the oxidized and nonoxidized samples containing NEPA are small and the data actually show the oxidized sample to be slightly better than the nonoxidized sample initially. AgeRite Geltrol is not drastically affected by the oxidizing agent. Polygard is more affected than AgeRite Geltrol or AgeRite NEPA but less than Stalite. Both samples containing Ethyl 702 showed poor stability, probably because of poor incorporation. All the data for the samples coagulated with NaNO_2 present are shown in Figure 2. This ranks the stabilizers in the following order:

- (1) AgeRite NEPA
- (2) AgeRite Geltrol
- (3) Polygard
- (4) Ethyl 702
- (5) AgeRite Stalite



TABLE IV

Evaluation of Stabilizers for SBR Coagulated under the Oxidizing Conditions
of SBR/Starch Xanthide Masterbatch Coagulations

Sample	Antioxidant	phr	NaNO ₂ phr	Mooney, ML-4										Change in Mooney Viscosity					
				After 105°C Air Oven Aging															
				Od	1d	3d	5d	7d	10d	14d	1d	3d	5d	7d	10d	14d			
1	None	--	--	22	81	94	100	Discontinued			59	72	78	Discontinued					
2	None	--	1.1	40	133	178	Discontinued				107	152	Discontinued						
3	Polygard	1.25	--	25	31	35	44	47	49	57	6	10	19	22	24	32			
4	Polygard	1.25	1.1	25	39	54	56	62	64	73	14	29	31	37	39	48			
5	AgeRite Geltrol	1.25	--	26	29	35	41	44	46	49	3	9	15	18	20	23			
6	AgeRite Geltrol	1.25	1.1	27	32	38	46	51	59	70	5	11	19	24	32	43			
7	AgeRite Stalite	1.25	--	27	31	43	43	46	46	54	4	16	16	19	19	27			
8	AgeRite Stalite	1.25	1.1	28	66	85	109	Stopped			38	57	81	Stopped					
9	AgeRite NEPA	1.25	--	27	30	35	36	41	51	51	3	8	9	14	24	24			
10	AgeRite NEPA	1.25	1.1	28	27	33	35	36	38	118	-1	5	7	8	10	90			
11	Ethyl 702	1.0	--	27	53	78	81	85	108	Stop	26	51	54	58	81	Stop			
12	Ethyl 702	1.0	1.1	27	44	59	62	66	78	88	17	32	35	39	51	61			
13	Starch Xanthate	5.0	1.1	28	77	98	130	Stopped			49	70	102	Stopped					



FIGURE 1

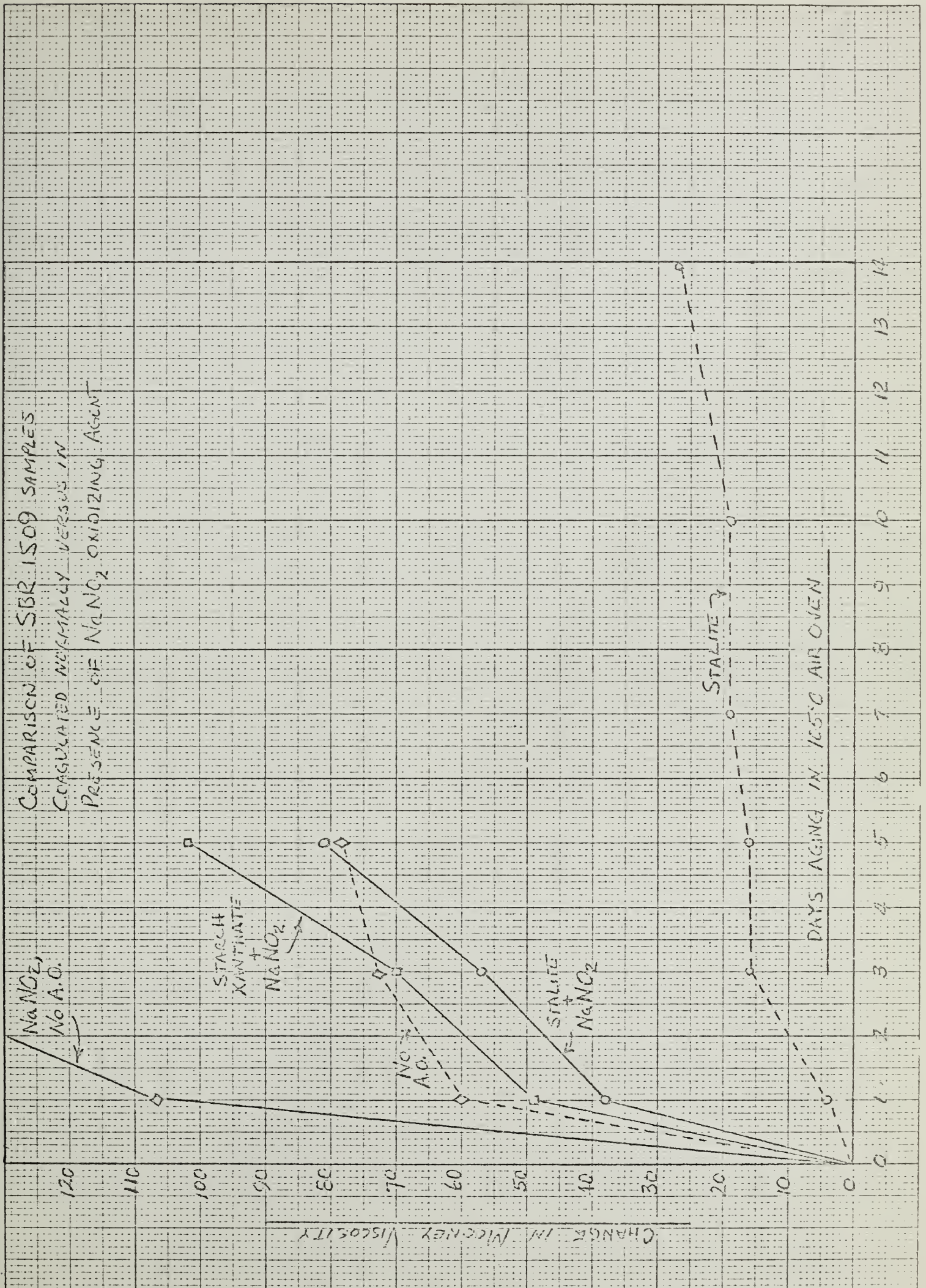
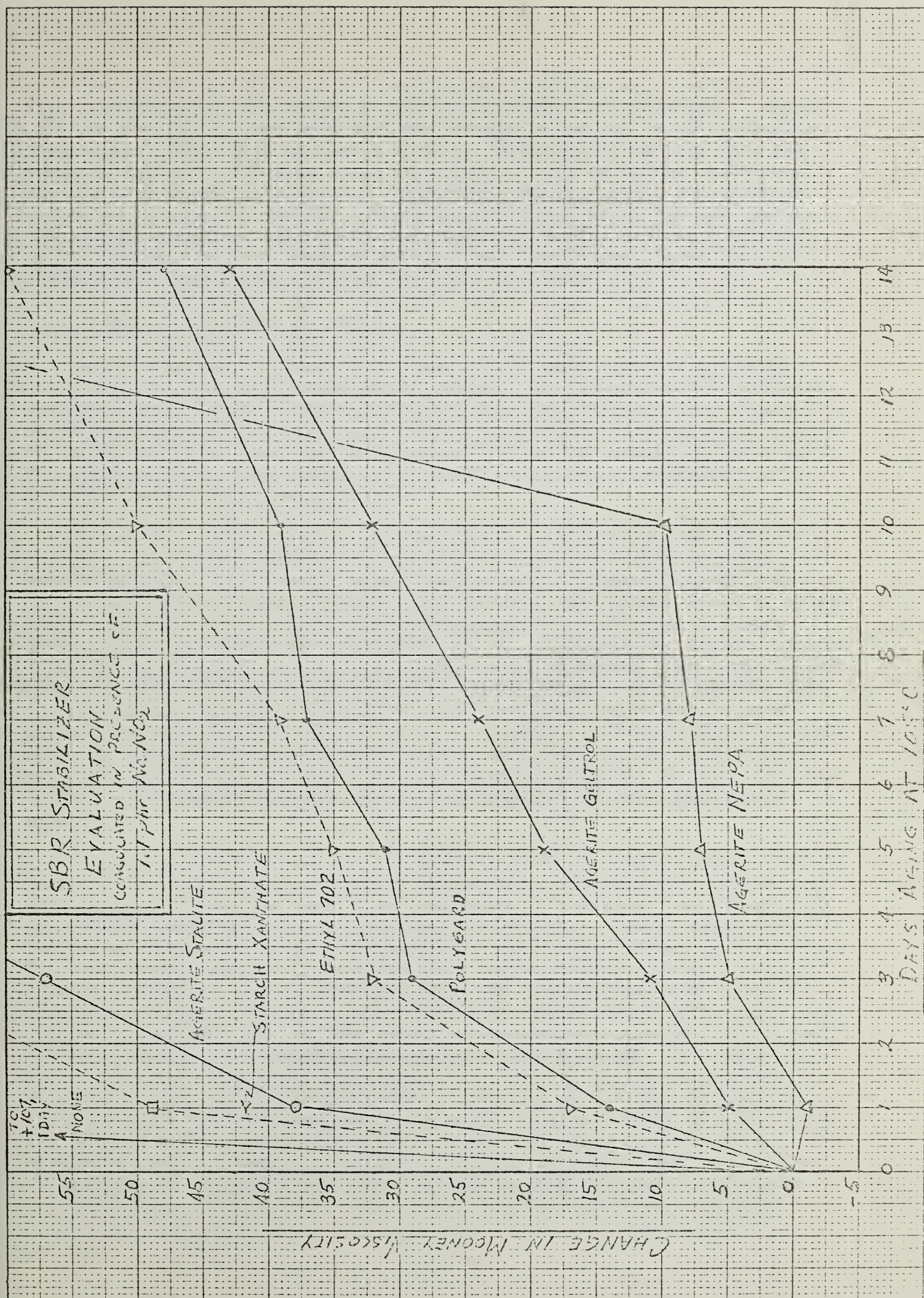


FIGURE 2





Two SBR 1503/45 phr starch xanthide masterbatches were coagulated with 1.25 phr stabilizer added to the rubber latex as an emulsion. AgeRite NEPA and AgeRite Geltrol were evaluated versus a control in which AgeRite Stalite was added after extrusion drying. The physical testing data are shown in Table V. No aging study was planned. The two latex stabilized samples were higher in viscosity (Rheometer minimum torque) and hardness and slightly lower in tensile. The presence of the stabilizer may reduce the polymer breakdown rate during the extrusion drying process. Addition of a stabilizer such as AgeRite NEPA to the latex before coagulation was recommended. Subsequent coagulations used this technique.

Bench Scale Composition Experiments

Several series of bench scale coagulations were prepared to study the effects of various compositional changes. The compositional variations included starch loading, xanthate degree of substitution, rubber Mooney viscosity, latex emulsifier, resorcinol/formaldehyde modification, extender oil level and type. The semi-continuous bench scale coagulation was used. The value of these experiments is clouded by the lack of reproducibility for these bench scale coagulations.

A series of masterbatches were prepared to evaluate various starch loadings and blending SBR/starch xanthide masterbatches with different starch loadings. If blending masterbatches with different compositions is successful, only several general masterbatch compositions would be necessary. Otherwise, many specialized masterbatches must be made for each application. Masterbatches containing 30, 45, 60 and 90 phr starch xanthide (0.08 DS) were coagulated. As the starch level increased, the crumb became more difficult to drain. The physical testing data for these samples and several blends are shown in Table VI. There appears to be little or no difference between the 30 and 45 phr masterbatches. Neither blending 30 phr and a 90 phr starch xanthide masterbatches nor blending the 90 phr starch xanthide masterbatch with SBR 1503 significantly affected the physical properties. Mechanical blending masterbatches after they are made seems practical.

A series of SBR/45 phr starch xanthide (0.07 DS) samples were prepared using latexes with different Mooney viscosities. The physical testing for this series is shown in Table VII. A portion of each latex was coagulated and dried without any reinforcing agents or fillers. These samples were compounded with SRF black for comparison. The data are shown in Table VIII. The tensile and modulus change for both starch xanthide and SRF black reinforced rubber as the Mooney increases. The lowest Mooney SBR (19 ML) yielded the lowest tensile in both the starch xanthide and SRF series. The remaining four SBR's in the SRF series had equivalent tensiles. The starch xanthide series had an optimum tensile with the 69 ML SBR. The higher Mooney SBR's gave slightly lower tensiles. In both series, the modulus increased as the SBR Mooney increased. The rate of increase was greater for the starch xanthide samples than the SRF samples. This, in part, might reflect the differences in compound viscosity as shown by the minimum Rheometer torque. Longer mill times to incorporate the black or a greater breakdown rate with black may have caused the lower compound viscosities with the higher SBR Mooney values. For an SBR/45 phr starch xanthide masterbatch the best balance of properties is obtained with a 50-70 ML polymer.



TABLE V

Evaluation of SBR 1503/45 phr Starch Xanthide Masterbatches
Stabilized with NEPA and Geltrol before Coagulation
Versus Stabilization after Drying

<u>Sample No.</u>	<u>45P17-2</u>	<u>47P17-5</u>	<u>47P17-6</u>
Stabilizer	Stalite	NEPA	Geltrol
Stabilizer Level, phr	1.25	1.25	1.25
Stabilizer Addition	after drying	Latex	Latex
<u>Compound No.</u>	<u>A39B</u>	<u>A39E</u>	<u>A39F</u>
Recipe, phr			
Masterbatch	145	145	145
Zinc Oxide	5.0	5.0	5.0
Stearic Acid	1.5	1.5	1.5
Altax	3.0	3.0	3.0
PBNA	1.25	1.25	1.25
Sulfur	2.0	2.0	2.0
<u>Rheometer, LS, 293°F</u>			
Torque, min.	2.9	4.0	4.0
Torque, max.	74	77	74
Scorch Time, min.	11.2	11.5	10.6
Cure Time, min.	24	26	26
<u>Stress-Strain, Cured at 293°F</u>			
Cure Time, min.	25	25	25
300% Modulus, psi	1250	950	900
Tensile, psi	1350	1150	1100
Elongation, %	330	420	390
Hardness, Duro A	63	69	67

Starch Xanthate: Hoosier Pearl Corn Starch
0.50 mole NaOH
0.08 D.S. (analyzed)

SBR 1503: 47 ML-4'-212°F
nominal 23.5% Bound Styrene
Fatty Acid Emulsifier



TABLE VI

Evaluation of SBR 1503/Starch Xanthide Masterbatches
Containing Different Starch Levels

<u>Compound No.</u>	<u>A39A</u>	<u>B</u>	<u>C</u>	<u>D</u>	<u>G</u>	<u>H</u>
Sample No.	45P17-1	45P17-2	46P17-3	46P17-4	Blend	Blend
phr Starch	30	45	60	90	45	45
<u>Compound Recipe</u>						
45P17-1	130	--	--	--	97.5	--
45P17-2	--	145	--	--	--	--
46P17-3	--	--	160	--	--	--
46P17-4	--	--	--	190	47.5	95
SBR 1503	--	--	--	--	--	50
Sundex 8125	--	--	20	60	--	--
ZnO	5.0	5.0	5.0	5.0	5.0	5.0
Stearic Acid	1.5	1.5	1.5	1.5	1.5	1.5
Altax	3.0	3.0	3.0	3.0	3.0	3.0
PBNA	1.25	1.25	1.25	1.25	1.25	1.25
Sulfur	2.0	2.0	2.0	2.0	2.0	2.0
<u>Rheometer, LS, 293°F</u>						
Torque, min.	2.4	2.9	2.3	1.0	3.0	4.3
Torque, max.	75	74	67	44	84	93
Scorch Time, min.	13.7	11.2	10.5	11.0	10.8	11.0
Cure Time, min.	33	24	23.5	23	24	30
<u>Stress-Strain, 293°F Cure</u>						
Cure Time, min.	30	25	25	25	25	30
300% Modulus, psi	1100	1250	1200	850	1450	1150
Tensile, psi	1350	1350	1550	1050	1550	1150
Elongation, %	370	330	420	450	330	300
Hardness, Duro A	59	63	62	57	68	71


Starch Xanthate: Hoosier Pearl Corn Starch
0.5 mole NaOH
D.S. = 0.08 (analyzed)

SBR 1503: 47 ML-4'-212°F



TABLE VII

Effect of SBR Mooney Viscosity on Properties
of SBR/45 phr Starch Xanthide Masterbatches

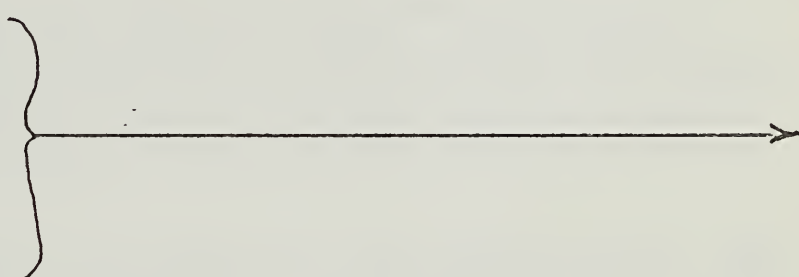
<u>Sample No.</u>	<u>33P13-1</u>	<u>33P13-2</u>	<u>34P13-3</u>	<u>34P13-4</u>	<u>35P13-5</u>
SBR Latex	1519	1503	1503+	1503+	1708
	--	--	1708	1708	--
Latex ML-4'	14	47	69	94	120
<u>Compound No.</u>	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>	<u>E</u>
Masterbatch	145				
ZnO	5.0				
Stearic Acid	1.5				
Altax	3.0				
AgeRite Powder	1.25				
Sulfur	2.0				
<u>Rheometer</u>					
Torque, min.	1.2	3.2	5.7	7.0	9.5
Torque, max.	73	69	82	86	93
Time, scorch	12	14	12	11	10
Time, 90% cure	33	36	37	36	34
<u>Stress-Strain, Cured 35' @ 293°F</u>					
200% Modulus, psi	1000	750	1000	1000	1200
300% Modulus, psi	1250	1300	1800	2150	--
Tensile, psi	1350	1750	2300	2150	2050
Elongation, %	350	370	360	300	290
Hardness, Duro A	68	60	63	63	63

Starch Xanthate: Hoosier Pearl Corn Starch
0.5 mole NaOH
0.07 DS

SBR Latex: nominal 23.5% Bound Styrene
Fatty Acid Emulsifier
Viscosity varied as shown.

TABLE VIII

Effect of SBR Mooney Viscosity on SBR/SRF Black Compounds

<u>Sample No.</u>	<u>35P13-6</u>	<u>36P13-7</u>	<u>37P13-8</u>	<u>37P13-9</u>	<u>38P13-10</u>
SBR Latex	1519	1503	1503+	1503+	1708
	--	--	1708	1708	--
ML-4'-212°	14	47	69	94	120
<u>Compound No.</u>	<u>27A</u>	<u>27B</u>	<u>27C</u>	<u>27D</u>	<u>27E</u>
Parts Recipe					
Rubber	100				
SRF	50				
ZnO	5				
Stearic Acid	1.5				
Altax	3.0				
PBNA	1.25				
Sulfur	2.0				
<u>Rheometer, LS, 293°F</u>					
Torque, min.	1.0	3.4	4.5	5.8	7.1
Torque, max.	47	62	68	82	86
Time, scorch	9.0	7.0	6.3	6.3	5.5
Time, cure	21	23	24	28.5	30.5
<u>Stress-Strain, 293°F Cure</u>					
Cure Time, min.	25	25	25	30	30
300% Modulus, psi	1300	1450	1600	1800	2000
Tensile, psi	2200	2750	2800	2750	2800
Elongation, %	500	520	500	440	400
Hardness, Duro A	62	63	65	65	67



Previous work in other laboratories indicated that better physical properties are obtained as the degree of substitution (DS) decreases. A series of SBR 1500/45 phr starch xanthide masterbatches were prepared to further evaluate these findings. A 10% corn starch slurry which was treated with 0.5 mole NaOH was reacted with various levels of carbon disulfide. The starch xanthate was blended with SBR 1500 latex and coagulated using the semi-continuous procedure. None of the coagulations gave a good crumb size. This was particularly true for the lower D.S. samples. The rosin emulsifier used in SBR 1500 is suspected as the cause of the poorer crumb size. Most of the bench scale work has used a fatty acid emulsifier or mixed fatty/rosin acid emulsifier. Visual observations indicate higher losses in the serum when the D.S. was decreased.

The physical testing data for this series are shown in Table IX. Several samples showed exceptionally good properties. Sample 40P14-3 gave excellent properties. The trend toward better physicals with reduced D.S. is evident. The physicals for the very low D.S. samples, however, were very erratic. The best balance of properties is obtained with 0.06-0.07 D.S. starch xanthate.

SBR 1500 (rosin emulsifier) has previously shown higher tensiles than other SBR's in starch xanthide masterbatches. Masterbatches based on SBR 1500 and SBR 1503 (fatty emulsifier) were prepared with and without the use of Nalco 107 (polyamine) as a coagulation aid. Each coagulation was further subdivided into air dried and Brabender extrusion dried sections. The SBR 1500 gives a crumb which is difficult to drain. Nalco 107 does not improve the crumb size of either the SBR 1500 or SBR 1503 masterbatches. Nalco 107 is not recommended for SBR starch masterbatch coagulations. The SBR 1503 without Nalco 107 gave the best coagulation crumb. The physical testing results (Table X) similar tensile properties except for one SBR 1500 masterbatch. The SBR 1500 showed the capability of excellent properties. The conditions needed to obtain these properties consistently are not known nor is the reason for the difference between SBR 1500 and SBR 1503 understood. The Nalco 107 does not affect physical properties except that it significantly increases the cure rate. This is not unexpected since this polyamine is known to accelerate the cure in other SBR products. Except for the one SBR 1500 masterbatch, extrusion drying did not affect tensile. The primary effect of extrusion drying in this case is making the material softer (lower hardness and modulus) and more homogeneous. Except for the one SBR 1500 masterbatch, extrusion drying did not affect tensile. The primary effect of extrusion drying in this case is making the material softer (lower hardness and modulus) and more homogeneous.

A series of SBR 1708/oil/starch xanthide samples were prepared. The level of Sunthene 380, a naphthenic extender oil was varied from 5 phr to 50 phr. The starch xanthide loading was varied to maintain a 45 parts SX to 100 parts rubber plus oil ratio. Two samples were prepared with higher starch xanthide loadings but the oil was withheld until compounding. Samples were also prepared with different oils. The physical testing data for these samples are shown in Table XI. The tensiles for all samples were very good, particularly since all the previous tensile data for SBR/50 oil/70 starch xanthide masterbatches are about 1100 psi. As expected, the tensiles decrease as the oil level increases (Samples A, B, C, D and G). There is no sacrifice in properties up to 10 phr oil. Beyond the 10 phr level, there seems to be a tendency to reduce tensile significantly with an overcure. Nonetheless, the generally good tensiles in this series was very encouraging.

TABLE IX

Effect of Degree of Carbon Disulfide Substitution on the
Physical Properties of SBR 1500/45 phr Starch Xanthide Masterbatches

9345	A	B	C	D	E
Sample No.	<u>39P14-1</u>	<u>39P14-2</u>	<u>40P14-3</u>	<u>40P14-4</u>	<u>41P14-5</u>
Degree of Substitution	0.114	0.078	0.068	0.048	0.032
CS ₂ Efficiency, %	91	78	82	72	65
<u>Rheometer, LS @ 293°F</u>					
Torque, min.	4.0	4.0	5.0	4.8	4.5
Torque, max.	60	72	72	67	71
Time, scorch	23	16.5	9.7	11	12
Time, cure	49	34	26	27	31
<u>Stress-Strain, Cured at 293°F</u>					
Cure Time, min.	50	35	30	30	30
300% Modulus, psi	1150	2400	1600	1450	1400
Tensile, psi	2100	2400	3000	2300-2800	2500-2900
Elongation, %	420	300	430	400	440
Hardness, Duro A	57	62	58	56	54

<u>Compound Recipe</u>	<u>phr</u>
SBR/SX Masterbatch	145.0
Zinc Oxide	5.0
Stearic Acid	1.5
Altax	3.0
PBNA	1.25
Sulfur	2.0

TABLE X

EVALUATION OF 45 PHR STARCH XANTHIDE MASTERBATCHES USING SBR 1500
AND SBR 1503, AIR DRIED VERSUS EXTRUDER DRIED

Compound '9867								
	A	B	C	D	E	F	G	H
Sample	52P21-1A	52P21-1E	52P21-2A	52P21-2E	53P21-3A	53P21-3E	53P21-4A	53P21-4E
SBR	1500	1500	1500	1500	1503	1503	1503	1503
Nalco 107	No	No	Yes	Yes	No	No	Yes	Yes
Drying	Air	Ext.	Air	Ext.	Air	Ext.	Air	Ext.
Rheometer, 293°F.								
Torque, Min.	18	6	36	7.5	10.3	4.7	9.0	5.5
Torque, Max.	135	72	164	88	117	85	122	94
Scorch Time	11	15	6.5	7.2	14	14	7	8.5
Time to T ₉₀	34	44	16	19.5	43	43	24	27
Physical Properties, 293°F. Cure								
300% Modulus	1600	1600	--	2900	--	1250	--	1500
Tensile, psi	1600	1600	1500	3100	1450	1350	1400	1550
Elongation, %	300	300	100	320	220	320	230	310
Durometer A	85	59	91	63	81	66	80	68

Extruder - Brabender

TABLE XI

Effect of Extender Oil Type and Level on Physical Properties
of SBR 1708/Oil/Starch Xanthide Masterbatches

Compound	A	B	C	D	E	F	G	H	I	J
Masterbatch Sample	17P9-1	17P9-2	18P9-3	18P9-4	19P9-5	19P9-6	20P10-1	20P10-2	21P10-3	21P10-4
Starch, phr	48	50	55	62	50	62	70	70	70	70
Oil, phr	5	10	25	37.5	0	0	50	50	50	50
Oil	Sunthene 380						Sunth. 380	Gulf NE 95	Sundex 8125	Sunpar 115
Oil Type							Naph.	Aromatic	Hi.Arom.	Paraff.
Masterbatch	153	160	180	200	150	162	220	220	220	220
Sunthene 380	--	--	--	--	10	37.5	--	--	--	--
Zinc Oxide	5)									
Stearic Acid	1.5)									
Altax	3.0)									
Sulfur	2.0)									
Cure Time @ 293°F	15'	15'	15'	15'	15'	30'	20'	20'	25'	20'
Modulus 200%, psi	1550	1350	--	--	--	--	--	--	--	--
Modulus 300%, psi	--	--	1900	1800	1900	600	1600	1300	2200	1300
Tensile, psi	2300	2300	2150	1950	2000	1500	1700	1750	2550	1500
Elongation, %	260	280	330	310	320	490	330	410	340	370
Durometer A	69	64	65	68	58	43	65	58	64	62
Cure Time @ 293°F	25'	25'	25'	25'	25'	40'	30'	30'	35'	30'
Modulus 200%, psi	1550	--	1350	1400	1100	--	--	--	--	--
Modulus 300%, psi	--	2500	--	--	--	700	1700	1400	2200	1300
Tensile, psi	2300	2500	1500	1600	1900	1400	1750	1700	2500	1500
Elongation, %	270	300	220	230	280	440	310	380	340	360
Durometer A	69	66	65	71	60	43	65	59	67	63

Starch: Hoosier Pearl Corn Starch Xanthate: 0.08-0.07 D.S. (estimated)
Coagulation: Semi-Continuous, 160°F, pH 4-5 SBR 1708: 120 ML-4'-212°F

Pilot Plant Coagulation Scale-Up

Despite some misgivings about the reproducibility of the bench scale coagulations, scale-up in the pilot plant was started. The pilot plant coagulation line flowsheet is shown in Figure 3. While the coagulation itself is continuous, the preparation of the starch xanthate and the latex blending were batch operations. The standard procedure allowed at least 30 minutes for the xanthate to form before the latex was added. The latex, antioxidant emulsion, and sodium nitrite solution were added to the starch xanthate solution and mixed for at least 30 minutes before coagulation was started. Because of the agitation in the blend tank, each coagulation run was limited to 50 pounds of product. The 100 gallon blend tank was agitated with an air driven turbine blade mixer. The blend tank was placed on a scale so materials could be weighed in and the discharge rate determined.

The Xantex was pumped with a Moyno Pump from the weigh/blend tank to the 25 gallon agitated coagulation tank. The coagulation serum pH was maintained by the constant addition of a dilute sulfuric acid solution. The acid flow rate was controlled automatically by a pH controller/indicator. The coagulator overflowed onto a shaker screen equipped with "grizzly bars" with 0.02 inch spacings. In most cases the spent serum was discarded. The wet crumb was dropped into a 25 gallon agitated wash tank with fresh water added continuously. The wash tank overflowed into a cheesecloth lined crumb box. When possible, additional water was drained from the crumb by wrapping the crumb in the cheesecloth and applying pressure manually. The crumb was air dried and rewet with 10-15% water. Some runs consisted of several coagulation variables which were sampled at the coagulator. The bulk of these runs were not always worked up beyond washing. Mechanically this arrangement worked reasonably well.

The initial pilot plant coagulations yielded extremely-fine (small) coagulation crumbs. These fines passed through and plugged the shaker screen and plugged the cheesecloth pores. The conditions which eventually seemed optimum were: (1) pH 3-4, (2) cool temperatures (80°F), and (3) minimum agitation in the coagulator. The initial portion of each coagulation indicated that the actual coagulation required some residence time. Crumbs were not formed immediately. During a run at least some of the new material coagulated as a coating on previously formed crumbs. If agitation was gentle this process caused crumb agglomerates to form. The agglomerates easily broke up with agitation.

Several attempts were made at increasing the coagulation crumb size. Sodium sulfate is naturally formed during coagulation through the neutralization of the sodium xanthate with sulfuric acid. The beginning serum did not contain the sodium sulfate concentration which will eventually build up in the coagulator. The addition of 0.9% sodium sulfate to the initial coagulation serum seemed to reduce the time needed to obtain a good crumb. Higher concentrations in the range of 2 to 3 times the natural level were not particularly advantageous. The addition of about 4% methanol to the coagulation serum seemed to reduce the mushiness of the coagulation crumb. This was not actively pursued because of the toxicological and flammability problems associated with methanol.



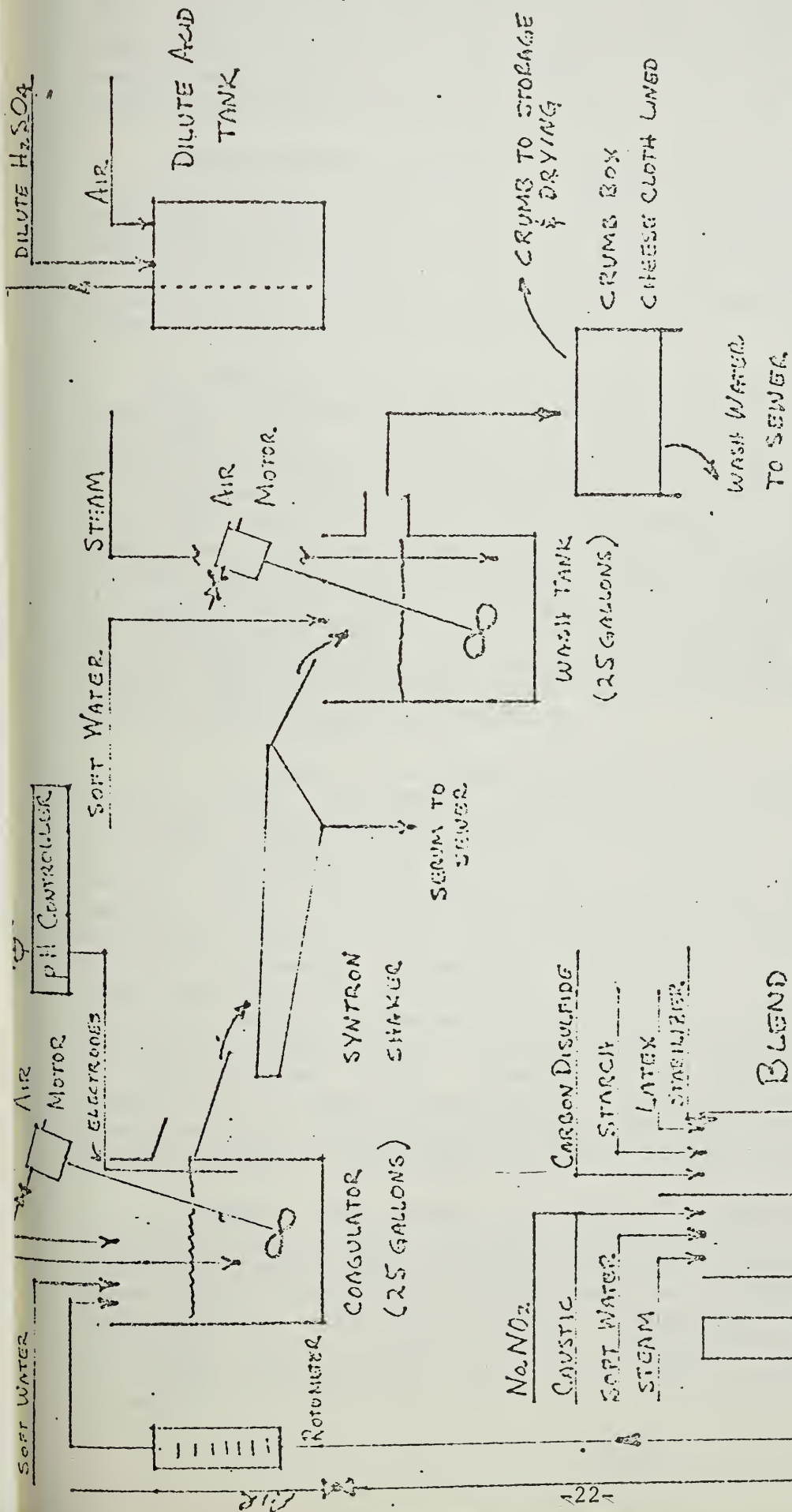


FIGURE 3

FLOW DIAGRAM OF CONTINUOUS
COAGULATION LINE FOR STARCH/RUBBER
MASTERBATCHES IN IDC PILOT PLANT

9-2-71
Frank Males

The physical properties for the continuously coagulated pilot plant samples were often disappointing. The better bench scale coagulations gave tensiles between 2000 and 2500 psi such as the typical data shown in Table XII. The continuously coagulated samples gave tensiles generally below 2000 psi - some were below 1500 psi. Tables XIII, XIV, and XV show physical testing data from several continuous coagulation runs. The tensiles ranged from about 1100 to 2200 psi for essentially the same composition. The lack of reproducibility as well as the low level of tensile were unacceptable. A re-examination of the coagulation fundamentals seemed appropriate.

The fundamental parameter in elastomer reinforcement is the particle size of the reinforcing material. The finer or smaller the particle, the better the reinforcement. Distribution or dispersion of the reinforcing agent is also critical. With carbon blacks these factors are generally related to bead breakdown. Other factors are "structure" (surface-to-volume or shape) and chemical bonding between the elastomer and reinforcing agent. The latter is the least documented.

The USDA work shows that the starch is the continuous phase at coagulation. Certainly during blending the starch xanthate solution is the continuous phase. The rubber latex particles are suspended in the starch solution even though the starch solids are less than the rubber solids. It is easy to conceive that during coagulation the starch coats or encases the rubber latex particle or rubber agglomerate. The rubber may not be coagulated in the traditional sense until after the starch coats the latex. It seems improbable that the starch could be coagulated without trapping or coagulating the rubber. This must be the case for the starch to be the discontinuous phase. Thus, the coagulation yields a product which has the phases inverted from the desired condition. This does NOT imply, however, that the coagulation conditions have no influence on the ultimate particle size or physical properties.

By necessity, the ultimate particle size is formed by mechanical action prior to curing. No chemical treatment of the crumb by itself will invert the phases. The available evidence indicates that the mechanical mixing during compounding is not sufficient to obtain a satisfactory starch particle size. The University of Akron discovered that extrusion processing partially dried starch masterbatches enhances physical properties. Electron microscopy verifies that a finer starch particle size is obtained with extrusion processing. Apparently, some moisture must be present. The role water plays has not been defined. Speculation is (1) water softens the starch for easier fragmentation and (2) water, shear, temperature (250-300°F) and maybe residual coagulation acid combine to break down the xanthate and/or the starch polymer itself. Breakdown of the xanthate or starch polymer appears to be a factor because higher degrees of carbon disulfide substitution give poorer physical properties. The higher DS would make the starch xanthate harder to break down because of greater cross-linking.

In summary, the problems are (1) which coagulation conditions give the finest starch particle or thinnest starch coating on rubber, and (2) what conditions promote phase inversion and starch breakdown? Ideally, the finest starch particle size would come from a complete coating of each latex particle. Any agglomeration or clustering of the latex particles (creaming) would increase the starch coating thickness. This would reduce the chance for obtaining a small starch particle during the phase inversion process.

TABLE XII
EVALUATION OF STARCH XANTHIDE/SBR 1503 MASTERBATCHES
COAGULATED AT DIFFERENT TEMPERATURES

Compd. 148	G	H	I
<u>Sample No.</u>	<u>66P25-1</u>	<u>66P25-2</u>	<u>67P25-3</u>
Starch Level	45	45	45
Coagulation Temp., °F.	100	125	150
Wet Crumb, Grams	1547	1410	1460
<u>Compound Recipe</u>			
Masterbatch	145	145	145
Zinc Oxide	5.0	5.0	5.0
Stearic Acid	1.5	1.5	1.5
PBNA	1.25	1.25	1.25
Altax	3.0	3.0	3.0
Sulfur	2.0	2.0	2.0
Cure Time @293°F, min.	45	45	45
<u>Physical Properties</u>			
300% Modulus, psi	1800	1800	1700
Tensile, psi	2200	2400	2100
Elongation	360	390	350
Hardness, Duro A	68	68	67

SBR 1503: nominal 23.5% Bound Styrene
nominal 50 ML Viscosity
Fatty Acid Emulsifier

TABLE XIII

Physical Testing of Pilot Plant 45 Starch Xanthide/SBR 1503
 Masterbatches Processed Through the Brabender

<u>Coagulation Run No.</u>	<u>3 & 4</u>	<u>5</u>	<u>7</u>	<u>Average</u>
Compound No. 914	K	L	M	
	Brabender			
<u>Rheometer</u>				
Torque, min.	6.5	6.0	5.8	
Torque, max.	67	65	63	
Scorch Time, min.	10	8.5	8	
Optimum Cure Time, min.	28	21	19	
<u>Physical Testing</u>				
300% Modulus (psi)	1500	1250	1350	1370
Tensile (psi)	1750	1500	1400	1550
Elongation, %	350	400	310	350
Durometer A	63	64	65	64

SBR 1503: nominal 23.5% Bound Styrene
 nominal 50 ML Viscosity
 Fatty Acid Emulsifier

TABLE XIV

Test Data for Pilot Plant Run 21
(45 phr SX/SBR 1503).

<u>Sample No.</u>	<u>21-1&2</u>	<u>21-3</u>
Compound No. 2047	10	11
Coagulation	Continuous, PP	Continuous, PP
Coagulation pH	2.5-3	4.5-5
Coagulation Temp., °F	140-120	100
Wash	Lab, Batch-----➔	
Drying	Air @180°F, Rewet, 3 Brabender Passes	

Monsanto Rheometer

(3° Arc, 3 cpm, 293°F)

Maximum Torque	80.1	78.0
Minimum Torque	6.3	6.9
Scorch Time (t ₂), Minutes	19.3	21.2
Optimum Cure (t ₉₀), Minutes	80.5	89.7
Cure Rate (k) X 100	3.8	3.4

<u>Stress-Strain</u>	<u>Min. Cured</u> <u>@293°F</u>	
Tensile Strength, psi	25	1270
	50	2210
	100	1980
Elongation, %	25	700
	50	410
	100	310
300% Modulus, psi	25	560
	50	1610
	100	1920
Shore A2 Hardness	25	54
	50	63
	100	64

- Notes: (1) 9.45% starch in SX
 (2) 0.057 D.S.
 (3) mushy crumb
 (4) 5.1 mg starch/ml coag. serum
 (5) 4.5 mg starch/ml wash serum

TABLE XV

Test Data for Pilot Plant Run 22
Using In-Line Mixer (45 SX/SBR 1503)

Sample No.	22-B	22-W	22-1	22-2	22-3	22-4	22-5
Compound No. 2368	7	8	9	10	11	12	13
Coagulation	Batch Lab	Cont. PP	Cont. PP	Cont. PP	Cont. PP	Cont. PP	Cont. PP
Coagulation pH	--	--	5	5	4	4	4
Wash	Batch Lab	Cont. PP	Batch Lab	Batch Lab	Batch Lab	Batch Lab	Batch Lab
Drying	Air Dried at 180°F, Rewet to 10%-15% Moisture, Brabender Extruded for 3 Passes						
Monsanto Rheometer							
(3° Arc, 3 cpm, 293°F)							
Maximum Torque	73.1	80.1	70.8	82.2	82.4	80.2	78.7
Minimum Torque	4.8	4.9	4.8	5.4	5.2	6.2	6.2
Scorch Time (t ₂), Minutes	27.9	15.3	16.7	14.8	14.4	18.2	20.3
Optimum Cure (t ₉₀), Minutes	77.0	38.1	39.9	37.9	39.3	58.9	59.9
Cure Rate (k) X 100	10.1	10.1	9.9	10.0	9.2	5.7	5.8
Min. Cured at 293°F							
Stress-Strain							
Tensile Strength, psi	UC	1560	1120	1310	1880	1890	1650
	1270	1670	1040	1180	1650	1650	1660
	1150	1610	980	1100	1600	1700	1520
Elongation, %	UC	400	580	450	460	670	800
	510	310	410	340	340	330	370
	300	350	330	330	330	310	300
300% Modulus, psi	UC	1110	660	1010	1320	900	740
	920	1480	850	1060	1500	1460	1410
	1150	1450	910	1050	1420	1650	1520
Shore A2 Hardness	UC	62	60	64	65	59	60
	60	65	65	67	65	65	66
	62	65	68	67	65	66	68
Specific Gravity	1.102	1.107	1.111	1.110	1.105	1.109	1.109

Notes: 1) Eppenbach In-Line Mixer was used in-line between blend tank and coagulator.
 2) Coagulation pH 3.5-5.0, Temp. @75°F, Recycle Serum only (No added Water).
 3) Standard NBS Compounding Recipe & Procedures

The extrusion process for phase inversion was studied at various time by both BFG and the USDA. In general, it was concluded that the extrusion process was essential to obtain satisfactory rubbery properties. The studies, however, indicated a rather broad range of conditions might be suitable (discussed in detail elsewhere in this report). This leaves coagulation as the critical step in obtaining a reproducible masterbatch with satisfactory properties.

Some bench scale work indicated that rapid coagulations would give higher tensile properties. Based on this information the pilot plant coagulation line was modified to get intimate mixing of the acid solution and the Xantex before entering the coagulator. The acid solution was added to the Xantex stream in a water educator or jet just prior to entering an Eppenbach In-Line Mixer. The coagulated mixture discharged into a small hold tank containing the pH electrodes and then overflowed into the coagulator. Later the hold-tank and coagulator were eliminated from the system and the Eppenbach discharged directly onto the shaker screen. The acid solution rate was then adjusted manually based on visual observation of the discharge.

This coagulation system worked well once the flow rates were properly balanced. The piping around the eductor plugged several times because acid backed up into the Xantex line. The coagulum that formed prematurely plugged the eductor nozzle. The crumb size was found to be a function of coagulation pH and coagulation temperatures. Cool coagulation temperatures around 80°F gave larger, firmer crumbs than coagulations at higher temperatures such as 100-120°F. The amount of fines passing through the shaker screen increased as the temperature increased. The best processing was obtained at coagulation pH's between 1.6 and 1.9. At higher pH's slight upsets in flow rates would give incomplete coagulation before discharging. At lower pH's a progressively finer crumb was obtained. While the fines passing through the shaker screen increased at lower pH's, the dissolved starch losses in the serum were reduced.

The masterbatches coagulated in the Eppenbach mixer yielded reproducible tensiles within the 2000 to 2500 psi range. The physical property data for the first five Eppenbach coagulation runs is shown in Table XVI. The data shows that the properties are insensitive to coagulation pH's within the range of 1.0 to 2.2, to coagulation temperatures between 72°F and 120°F, and to acid solution concentration between 2.5 and 10%. As might be expected, the wash pH affects the cure rate.

Because relatively good properties can be obtained consistently, the Eppenbach In-Line coagulation process was adapted as the standard.

TABLE XVI

Physical Properties of Five Pilot Plant Coagulations Using Eppenbach Mixer for Coagulation

Run No.	E-1	E-2	E-4	E-4	E-4	E-5	E-5	E-5	E-6	E-6	E-6
Sample No.	D	ABC	2W	3W	5W	3&4W	6&7W	1	3	6	
Coagulation pH	1.5-2.0	1.5	1.6	2	2	2	1	1.5	1.8	2.2	
Acid Conc., %	10	5	5	5	5	2.5	2.5	5	5	5	
Coag. Temp., °F	80	80	80	80	100	80	80	72	100	120	
Wash Water pH	--	--	--	--	--	2.2	1.8	2.5	3.3	2.7	
Drying	Brabender										
Rheometer, 3°, 3 cps, 293°F											
Max. Torque	71.5	71.5	78.5	75	76.5	73.5	75	64.5	64	75.5	
Min. Torque	5.7	6.2	6.8	6.2	6.0	6.0	7.0	5.3	6.8	5.5	
Scorch (t ₂), min.	23.5	18.0	22.8	21.2	22.5	21.0	22.8	15.3	16.3	15.2	
Optimum Cure(t ₉₀), m.	70.5	74.2	69.0	60.7	70.0	60.5	86.8	44.0	33.4	43.2	
Cure Rate	4.9	4.1	5.0	9.1	4.8	5.8	3.6	8.0	13.5	8.2	
Stress-Strain, Control Recipe, 293°F											
300% Modulus, 25	280	550	400	750	240	350	270	650	1000	1070	
(psi)	50 1070	1000	1600	1580	1310	1400	1120	1150	1750	1730	
	100 1680	1440	1970	1800	1860	1900	1500	1320	1860	1810	
Tensile,	25 1200	2070	910	2080	600	880	720	2250	2060	1540	
(psi)	50 2380	2110	2360	2180	1970	2040	2300	1950	1750	1920	
	100 2030	1860	2090	1940	2320	2250	1910	1750	1860	1970	
Elongation,	25 720	750	590	650	820	640	660	590	490	380	
(%)	50 500	510	400	380	400	380	500	400	300	320	
	100 340	380	310	320	350	350	350	350	300	320	
Hardness,	25 52	54	55	55	50	53	54	54	58	56	
(Duro A)	50 58	58	61	60	57	59	58	58	60	60	
	100 60	62	64	62	60	63	62	60	60	63	

Composition: 45 phr SX/SBR 1503

CS₂: 0.1 mole/mole starchNaNO₂: 0.1 mole/mole starch

SX Conc.: 8%

Extrusion Processing

As described elsewhere in this report, the coagulation yields rubber dispersed in a continuous starch phase. Extrusion processing or extrusion drying of starch masterbatches containing 8 to 20% moisture was found to enhance the masterbatch physical properties by the University of Akron. The reason, which was not fully explored by the University of Akron, is that a better or more complete phase inversion is obtained compared with no mechanical action prior to compounding. Non-extrusion processed starch/SBR masterbatches yield stiff, boardy, hard, short (low elongation) compounds which visually show gross non-homogeneity. Such compounds are not suitable for any or very many rubber applications. Extrusion processed samples, by contrast, gave softer, more rubbery compounds. Although the tensiles were sometimes similar, tensile is not the only rubber property criteria and, in fact, it may be less important than other properties. Thus, extrusion processing starch masterbatches is necessary to obtain a satisfactory product.

With the important advantages associated with extrusion processing, it naturally required further study. Unfortunately, the early attempts were plagued with the unrecognized variability of the coagulation process at that time. Many of the experiments involving extrusion processing variables must be viewed with this background.

The extrusion processing procedure used for standard bench scale coagulations and control type pilot plant samples was three passes through a 25/1 L/D Brabender laboratory extruder with a spaghetti die (7-1/32 inch holes). The feed zone and second zone temperatures were 257°F, the discharge zone temperature was 300°F. These conditions were rather arbitrarily set by the University of Akron and USDA laboratory. For cross reference and cross checking purposes these conditions were used as standard.

Since the USDA laboratory in Peoria was conducting a statistically designed set of experiments using the Brabender, BFG did not duplicate their effort. Two other laboratory extruders were evaluated plus the pilot plant scale V.D. Anderson Expander Dryer. The NRM (National Rubber Machinery Company) extruder has a short 2.2/1 L/D ratio which is used by many rubber extruders. A 1/4 inch round die was used on this one-inch diameter screw extruder. Table XVII shows the data for several experiments using the NRM and for Brabender and air dried only controls. The NRM and Brabender seem to give similar results despite the shorter residence time in the NRM extruder. A single pass does not give suitable physicals consistently.

A large quantity of 45 phr starch xanthide masterbatch was prepared. The bulk of the masterbatch was processed with one pass on the NRM extruder. Smaller samples were processed with two passes in the NRM and three passes in the Brabender. The larger batch was compounded both in a Banbury and on a mill. The smaller samples were mill mixed. These data (Table XVIII) show little difference between the extrusion conditions. The Banbury mix, however, showed poorer physical properties than the mill mixed samples. Shear conditions, temperatures, and residence time differences could be responsible for these variations.



TABLE XVII

Effect of Various Drying Conditions on SBR 1503/
Starch Xanthide Masterbatches

Sample 44Pl6-	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>7</u>
Extruder Type	--	Brabender	Brabender	NRM	NRM	NRM	NRM
No. Passes		1	3	1	2	1	3
Extruder, °F		255	255				
Die Temp., °F		300	300	220	1) 220 2) 283	283	283
Screw Speed, RPM		100	100	40	40	40	40
Air Drying Temp., °F	180-200	180-200	--	180-200	180-200	180-200	--
Die Configuration		1/32" round	1/32" round	1/4" round	1/4" round	1/4" round	1/4" round
No. Dies		7	7	1	1	1	1
% Volatile Matter*	67.3	14.1	2.0	10.2	12.6	7.5	6.3
Compound No.	<u>A38A</u>	<u>B</u>	<u>C</u>	<u>D</u>	<u>E</u>	<u>F</u>	<u>G</u>
<u>Rheometer, LS, 293°F</u>							
Min. Torque	9.5	3.2	3.8	4.5	3.8	3.5	3.5
Max. Torque	119	60	80	61	49	60	61
Scorch Time, min.	9.0	13.0	12.5	10.8	10.0	10.0	10.5
Cure Time, min.	30	50	34	26	26	26	29
<u>Stress-Strain, 293°F Cure</u>							
Cure Time, min.	30	50	30	30	30	30	30
200% Modulus, psi	1700	1300	1050	1100	1000	1100	1050
300% Modulus, psi	--	--	1450	--	--	1650	1550
Tensile, psi	1700	1300	1650	1400	1300	1750	1650
Elongation, %	200	200	400	260	250	320	310
Hardness, Duro A	84	68	65	68	66	67	64
Appearance	Spotty	Very Spotty	Uniform	Very Spotty	Very Spotty	Uniform	Uniform
Compound Recipe	<u>phr</u>						
Masterbatch	145						
Zinc Oxide	5.0						
Stearic Acid	1.50						
Altax	3.00						
PBNA	1.25						
Sulfur	2.00						
		Starch Xanthate: Hoosier Pearl Corn Starch 0.5 mole NaOH 0.0 D.S.					
		SBR 1503: 47 ML-4'-212°F					
		Extruder Feed: Air dried to about 20% moisture					

* After extrusion but before air drying

TABLE XVIII
EVALUATION OF DRYING METHODS AND COMPOUNDING MIXERS FOR
45 PHR STARCH XANTHIDE/SBR 1503 MASTERBATCHES

Compound No. 298 Masterbatch 72P27	<u>A</u> 1A	<u>B</u> 1A	<u>C</u> 1B	<u>D</u> 2
Drying Conditions After Air Drying to 10-20% Moisture				
Extruder type	NRM	NRM	NRM	Brabender
Speed, RPM	40	40	40	100
Barrel Temp., °F	270	270	270	257
Die Temp., °F	310	310	310	302
Number of Passes	1	1	2	3
Compound Recipe				
Masterbatch	145	145	145	145
Zinc Oxide	5	5	5	5
Stearic Acid	1.5	1.5	1.5	1.5
PBNA	1.25	1.25	1.25	1.25
Altax	3.0	3.0	3.0	3.0
Sulfur	2.0	2.0	2.0	2.0
Mixer	Mill	Banbury	Mill	Mill
Rheometer: 3 cps, 3°, 293°F				
Torque, min.	5.8	5.0	5.6	6.5
Torque, max.	75	66.5	72	110
Scorch Time (t ₂)	10.6	10.6	10.7	11.5
Cure Time (t ₉₀)	26	26	28	33
Stress-Strain: 293°F cure, 30 minutes				
300% modulus, psi	1550	1450	1500	1600
Tensile, psi	1650	1450	1700	1750
Elongation, %	350	300	360	350
Durometer A	77	76	77	76



An 0.8 inch Welding Engineers dual worm extruder was also tried. Barrel temperatures and worm speeds were varied. The 45 phr starch masterbatch was ground in a Fitzmill and wet with 15% water. The crumb was free-flowing enough to feed the extruder feed hopper. Only a single pass was used. Since the vacuum vent did not have a condenser in-line, it did not work properly. At the end of the run the vent was almost completely plugged. The primary objective of this trial was to study feeding characteristics, rates, and torque requirements to determine if further work at the Welding Engineers laboratory would be practical. None of the samples were completely dried by the extruder. After further air drying all the samples were compounded. In general, the samples processed with the Welding Engineers extruder were only slightly poorer than the three pass Brabender control (Table XIX). Although the data indicated further work with Welding Engineers should proceed, there was no follow up because of coagulation problems.

The V.D. Anderson Expeller/Expander drying system is a popular mechanical dryer in the synthetic rubber industry. The Independence Technical Center has a "Model" Anderson system which is the smallest produced. In our judgment, the Dewatering Expeller would be ineffective with the starch masterbatch coagulation crumb. No experiments were made with the Expeller.

The initial trials used 45 phr starch xanthide/SBR 1503 masterbatches made in the pilot plant. Several coagulation runs were combined to obtain enough material. The masterbatch was air dried at 180°F and re-wet with about 10-15% water and allowed to soak at least 16 hours.

The controlled variables for the Expander are: (1) screw speed, (2) die configuration (number and size), and (3) steam, water, or neutral on the barrel jacket. The die temperature and the temperature near the end of the screw are also recorded.

The first run was made with seven 1/8-inch round hole dies and 150 rpm. The barrel temperature quickly rose from 260 to over 400°F. The product was burned and gave off a foul odor. It was obvious that the die area should be increased. No product was retained. After cleaning, the dies were changed to five 1/4-inch round holes and the speed reduced to 100 rpm. The temperature started to rise rapidly again. Cooling water was put on the barrel jacket. The temperature averaged 310°F and ranged up to 320°F. The masterbatch was dark grey but not burned. Some additional water was added to some of the masterbatch which brought the temperature down and some lighter material was obtained. The discharge also had a higher moisture level. The bulk of Run 2 was retained. For Run 3, the dies were five 1/4-inch round holes plus two 1/8 x 3/8-inch slots; the screw speed was again 100 rpm. Cooling water was still needed on the barrel jacket. When the temperature rose over 300°F, the masterbatch turned grey. Most of Run 3 was made at 290-300°F. Higher moisture feed gave lower barrel temperatures and higher moisture in the finished product. The Run 3 rate was 220 pounds per hours; the die plate was 340°F (steam on). Run 3 was divided into two sections: A Section was the initial, dryer portion while B Section had higher moisture. In both cases, the drying was finished in an air drier at 180°F and the masterbatch retained.

Table XIX

Avon Lake Trial of the 0.8 inch Welding Engineers Dual
Worm Extruder for Starch Masterbatches

<u>Run</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>4/5</u>	<u>Control</u>	
Speed, RPM	50	75	75	75	165	50	Trans-	3-Pass	
Torque, in-lb.	42	50	50	42	55	33	ition	Brac-	
Rate, Gm/Min.	32	56	56	52	121	31	Run 4	bender	
Zone 2 Temp., °F	235	245	245	285	265	275	to	250	
Zone 3 Temp., °F	240	245	250	303	300	308	Run 5	250	
Zone 4 Temp., °F	245	245	285	315	315	290		300	
Zone 5 Temp., °F	245	245	278	275	275	275			
Vacuum Vent, in Hg	16	5	0	0	0	0		0	
Stock Temp., °F	270	295	300	340	350	330			
% Moisture	4.7	5.7	5.2	2.4	5.1	1.7			
<u>Compound 1261</u>	<u>C</u>	<u>D</u>	<u>E</u>	<u>F</u>	<u>G</u>	<u>H</u>	<u>I</u>	<u>B</u>	<u>Avg.</u>
									<u>W.E.</u>
<u>Rheometer</u>									
Torque, min.	6.4	6.5	6.2	6.2	6.7	7.2	6.5	5.8	
Torque, max.	87	87	86	85	78	91	82	82	
Scorch, Δ 2	14	14	14	15.5	16	14	15	14.5	
Cure Time, t ₉₀	41	40	41	45	47	42	46	43	
<u>Physical Testing, Cured 45' at 293°F</u>									
300% Modulus, psi	1150	1200	1100	1100	1000	1150	1150	1250	1120
Tensile, psi	1300	1500	1300	1350	1200	1150	1400	1450	1310
Elongation, %	330	410	380	400	380	300	350	370	360
Hardness, Duro A	67	66	65	67	62	69	63	64	65.7

The physical testing results for the retained Anderson samples is shown in Table XX. Also shown are the results of three pilot plant masterbatches processed through the Brabender. The Anderson trials included these masterbatches. The average Anderson properties are slightly poorer than the average Brabender properties.

The Anderson Expander has been used for processing all but one of the pilot plant lots used in compounding evaluations. While the results generally are slightly poorer with the Anderson versus the three pass Brabender control, it was the only practical method of processing the larger pilot plant quantities. Some additional comparisons between Brabender and Anderson processing are shown in Table XXI.

Some differences between the Brabender and Anderson might be caused by variations in feed preparation. The wet masterbatch for the Brabender was milled to obtain a sheet which was cut into strips. The moisture is well distributed in the sheet. For the Anderson the airdried chunks were rewet in a drum but were not processed any further before feeding the extruder. The moisture was not well distributed in this case. One pass versus three pass Brabender processing was evaluated. The one pass samples were air dried after extrusion. The data indicate that about half the one pass samples were equivalent to their three pass counterparts. The other half show poorer properties for the one pass samples.

In conclusion, extrusion processing is essential in obtaining satisfactory physical properties but the properties are insensitive to a wide range of equipment and conditions. The Anderson Expander is an acceptable piece of equipment for the extrusion processing step.

Physical Testing of Piloe Plant 45 Starch Xanthide/SER 1503
Masterbatches Processed Through the Brabender vs. the Anderson Expander

Coagulation Run No.	3 & 4	5	7	Average	Anderson Run	2	3A	3B	Average
Compound No. 914	K	L	M		Compound 1523	R	S	T	
	Brabender			----->	Drying				
Rheometer									
Torque, min.	6.5	6.0	5.3			8.8	7.1	5.9	
Torque, max.	67	65	63			78	82	98	
Scorch Time, min.	10	8.5	8.0			15	11.5	13	
Optimum Cure Time, min.	28	21	19			46	30	34	
Physical Testing									
300% Modulus (psi)	1500	1250	1350	1370		1300	1300	1250	1280
Tensile (psi)	1750	1500	1400	1550		1300	1550	1400	1420
Elongation, %	350	400	310	350		300	400	340	340
Durometer A	63	64	65	64		67	71	69	69

TABLE XXI
Comparison of Laboratory Brabender Extrusion Processing Versus
Pilot Plant Anderson Expander Processing

Sample No.	Run 23/24	Run 24	Lot A	Lot B	Lot C	Lot D	Lot H
SX, phr	50	50	45	45	30RF	55	30RF
Oil, phr	10	10	--	--	--	25	--
Latex	1708	1708	1503	1708	1503	1708	1032
Drying	SBR	SBR	SBR	SBR	SBR	SBR	NBR
	VDA	BRAB.	VDA	BRAB.	VDA	BRAB.	VDA
Compound No.	2731-2	2369-9			4151-3	4150-3	4586-7
Rheometer, 3°, 3 cps, 293°F							
Max. Torque	93.1	95.5	56.5	88.5	64	73	30
Min. Torque	15.1	13.3	5.3	6.0	5.5	6.0	3.4
Scorch (t ₂), min.	10.3	10.9	16.7	19.0	20.0	22.1	10.1
Optimum Cure (t ₉₀), min.	36.7	33.2	45.0	62.0	83	87	22.6
Cure Rate	8.7	10.3	8.1	5.3	3.6	3.5	18.4
Stress-Strain, Control Recipe, 293°F							
300% Modulus	25'	1500	850	610	540	280	820
(psi)	50'	1350	1270	1180	920	950	850
	100'	1220	1300	1440	1240	1370	850
Tensile(psi)	25'	1560	1600	1520	1170	710	1920
	50'	1400	1850	1810	1380	1610	1780
	100'	1360	1670	1720	1550	1370	1800
Elongation (%)	25'	350	490	800	600	700	540
	50'	350	400	500	370	420	520
	100'	330	370	370	350	300	530
Hardness (Duro A)	25'	62	59	57	60	57	62
	50'	67	63	63	63	60	62
	100'	68	63	66	62	65	62

Note: Lot G, a 30 phr SX/Hycar 1032 Masterbatch, was air dried.

Electron Microscopy

At several points in this report the importance of the final starch particle size distributed in the rubber matrix is discussed. While previous workers imputed the fine starch particle size, no one demonstrated this property experimentally. The electron microscope was found to be a suitable method of determining the physical characteristics of the starch in rubber.

Several of the photo-micrographs are included in this report to indicate the various conditions encountered. Figure 4 shows a 45 phr SX/SBR 1500 Brabender processed laboratory coagulation sample. The very fine particle size shown is reflected in the 3100 psi tensile obtained from this sample. It is one of two samples showing 3000 psi or higher tensile in this project. The air-dried counterpart of this sample is shown in Figure 5. Note that this is fine particles of rubber dispersed in starch. The 1600 psi tensile may be more of an indication of starch properties than rubber properties. Figure 6 shows a 45 phr SX/SBR 1503 air-dried masterbatch. Again, this is rubber in starch, except the rubber particles are much larger for SBR 1503 than SBR 1500. Figure 7 shows the Brabender processed sample based on SBR 1503. The starch particles are considerably larger than those shown in Figure 4 and this is reflected in the 1350 psi tensile. Figure 8 shows a 45 phr SX/SBR 1503 Brabender process sample which had 2400 psi tensile. Note that while there are many fine discreet starch particles, there are also zones of rubber in starch dispersed throughout. Also, some starch particles contain a core of rubber. Other electron photomicrographs show many variations between the extremes shown here. The tensiles generally correlate with the particle size shown in the photomicrographs.

This set of photos shows the value of the extrusion processing step. It also gives an indication that variables other than extrusion process may affect the starch particle size and tensile. If the coagulation gives large particles of starch and rubber, the extrusion processing step cannot easily reduce the particle size to where it can contribute toward reinforcement. The SBR 1500 masterbatches seem to give higher tensiles than SBR 1503. The electron photomicrographs suggest that the SBR 1500 yields finer, better distributed particles during coagulation compared with SBR 1503. The primary difference between them is that SBR 1500 uses a rosin emulsifier whereas SBR 1503 uses a fatty emulsifier. Unfortunately, the SBR 1500/starch masterbatches are very difficult to dewater. The coagulation crumb is very small, tends to hold more water and to give a cloudier serum than SBR 1503/starch masterbatches. The choice has generally gone with the easier processing SBR 1503.

Figure 9 shows a 45 phr SX/SBR 1503 Brabender processed sample taken from an Eppenbach In-Line pilot plant coagulation. The tensile for this sample was 2100 psi, about average for this type coagulation.

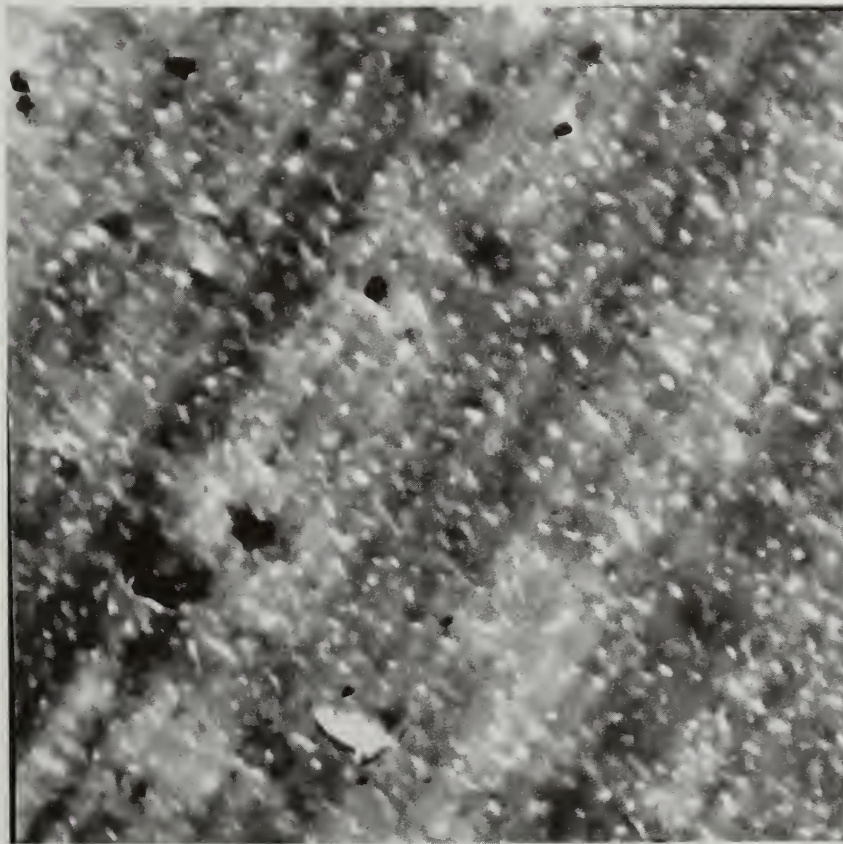


FIGURE 4

Electron Photomicrograph

Magnification: 12,500X
 Compound No.: 9867D
 Composition: 45 phr SX/SBR 1500
 Coagulation: Lab
 Drying Process: Brabender Extruder
 Rubber Properties
 Tensile: 3100 psi
 Hardness: 63

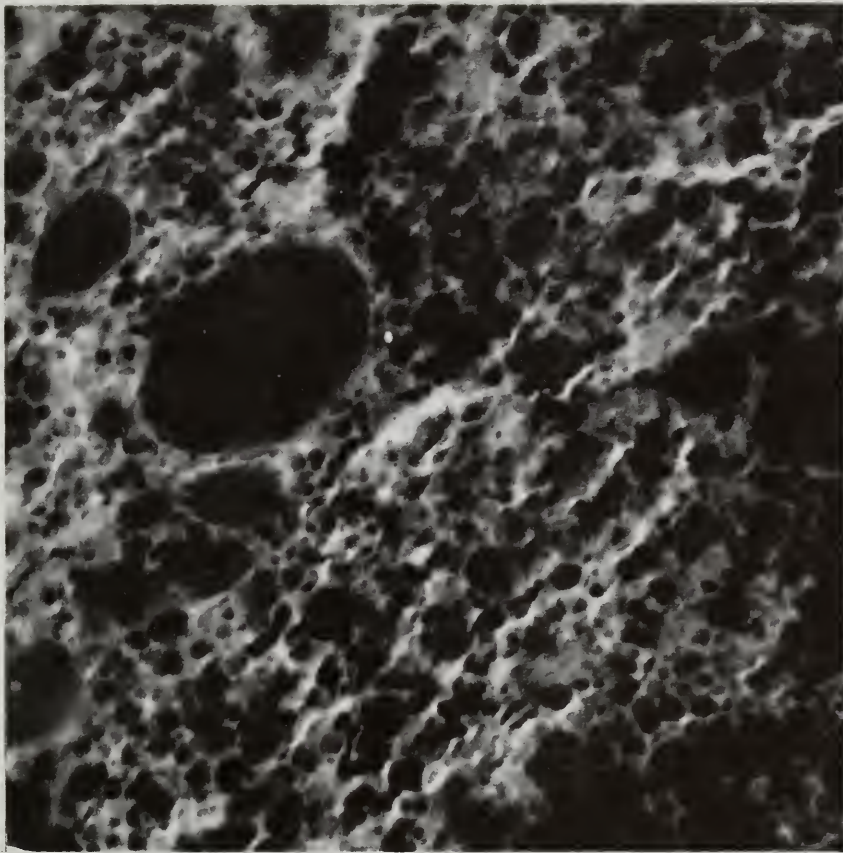


FIGURE 5

Electron Photomicrograph

Magnification: 15,000X
 Compound No.: 9867A
 Composition: 45 phr SX/SBR 1500
 Coagulation: Lab
 Drying Process: Air Only
 Rubber Properties
 Tensile: 1600 psi
 Hardness: 85

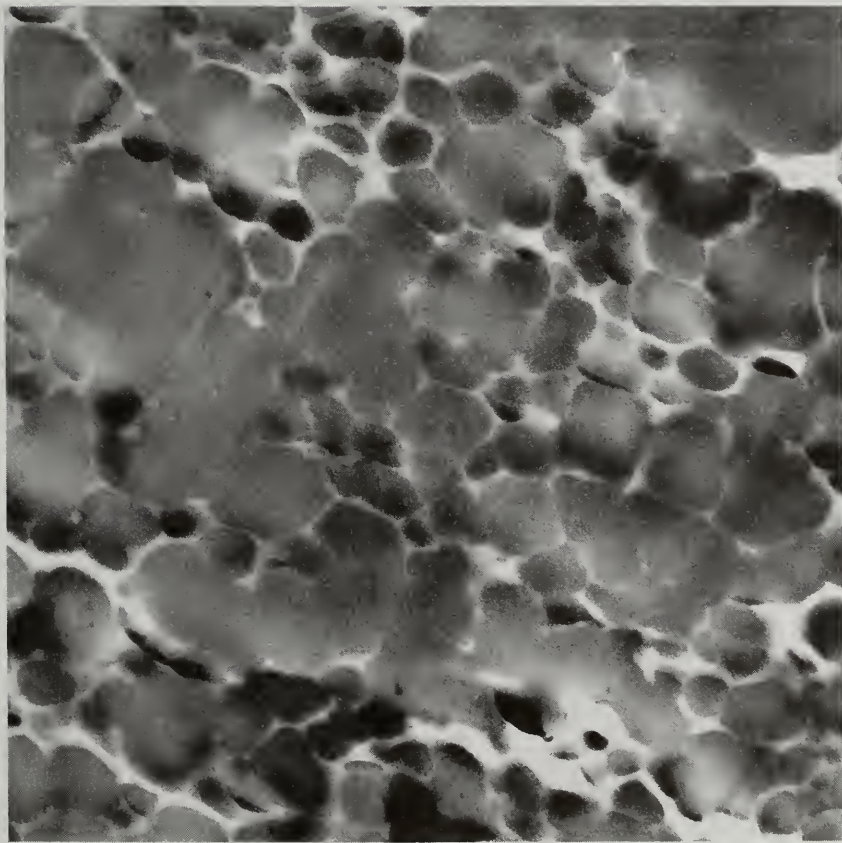


FIGURE 6

Electron Photomicrograph

Magnification: 15000X
 Compound No.: 9867E
 Composition: 45 phr SX/SBR 1503
 Coagulation: Lab
 Drying Process: Air Only
 Rubber Properties
 Tensile: 1450 psi
 Hardness: 81



FIGURE 7

Electron Photomicrograph

Magnification: 12,500X
 Compound No.: 9867F
 Composition: 45 phr SX/SBR 1503
 Coagulation: Lab
 Drying Process: Brabender Extruder
 Rubber Properties
 Tensile: 1350 psi
 Hardness: 66

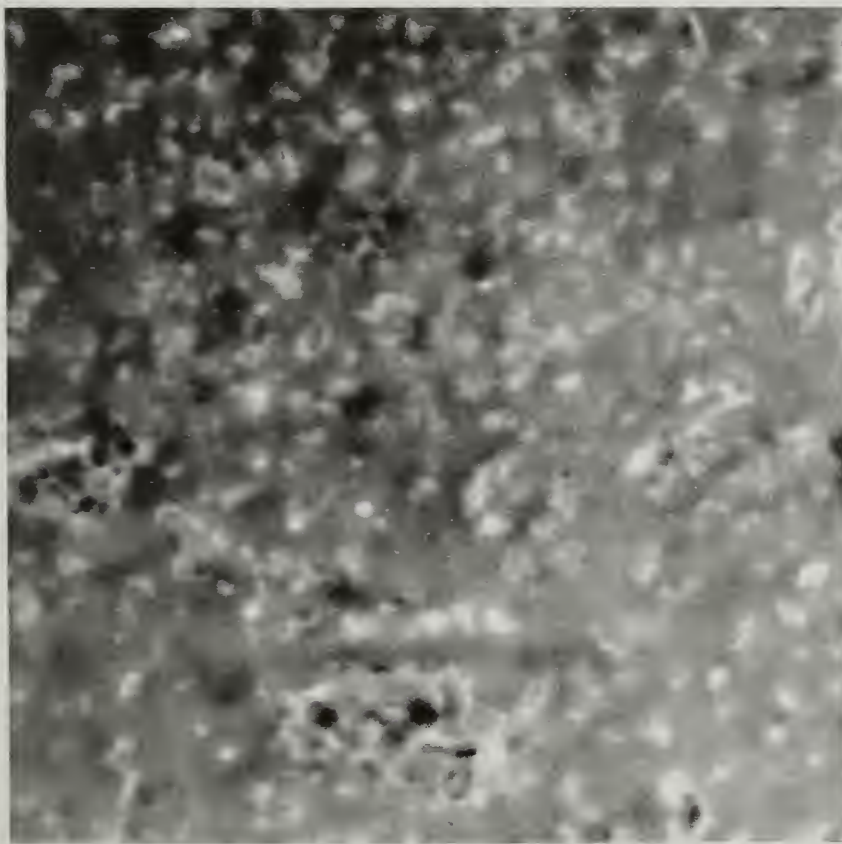


FIGURE 8

Electron Photomicrograph
 Magnification: 15000X
 Compound No.: 148H
 Composition: 45 phr SX/SBR 1503
 Coagulation: Lab
 Drying Process: Brabender Extruder
 Rubber Properties
 Tensile: 2400 psi
 Hardness: 68

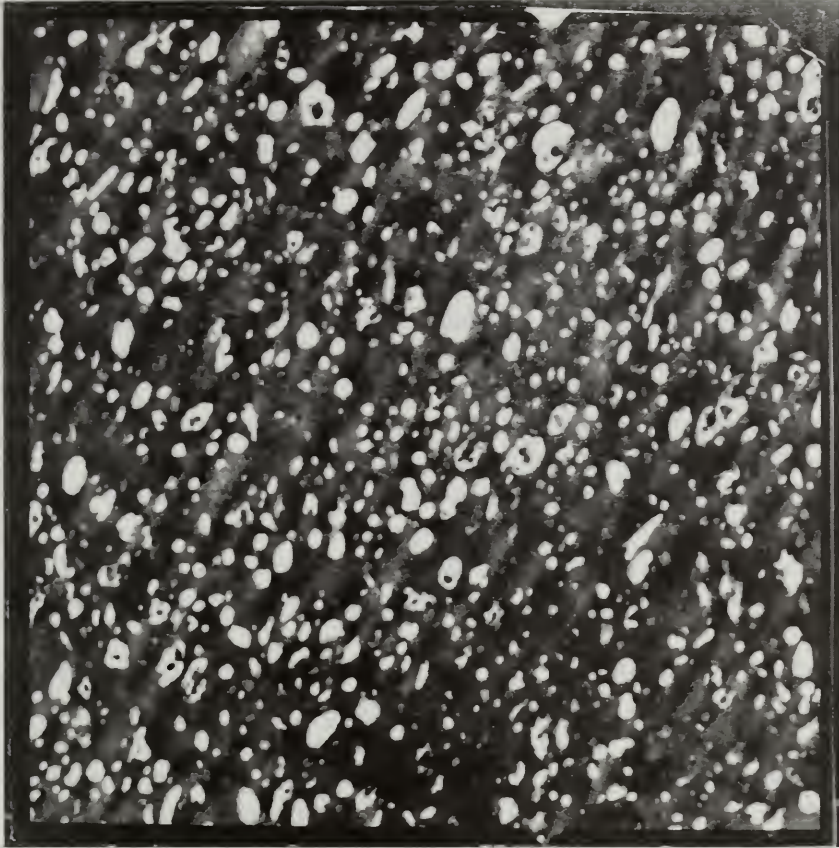


FIGURE 9

Electron Photomicrograph
 Magnification: 8200
 Compound No.: E-2ABC
 Composition: 45 phr SX/SBR 1503
 Coagulation: Eppenbach, Pilot Plant
 Drying Process: Brabender Extruder
 Rubber Properties
 Tensile: 2110 psi
 Hardness: 58

Flowsheet and Cost Calculations

A flowsheet (Figure 10) was drawn for a 5,000 lb./hr. finishing line for a 45 phr SX/SBR masterbatch. This rate is equivalent to about 36,000,000 pounds per year. A continuous process was chosen since it represents the most economical approach. Several of the processes shown have not been demonstrated but are thought to be feasible. One of the important assumptions is the continuous process for starch xanthation with minimal hold-up time. Filtration studies have been limited to rather crude bench scale experiments. Also, the operation of a continuous air dryer has not been demonstrated. In the batch air dryer some problems with crusting, uneven drying and sticking have occurred. The flow sheet shows the tremendously large amount of water which must be removed from the filtered masterbatch in the air dryer. For the starch masterbatch 14,460 pounds per hour water must be removed whereas for a black masterbatch or non-pigmented rubbers only 880 pounds per hour must be removed per 5000 pounds produced. Another area which requires more investigation is the removal and disposal of the toxic nitrogen oxides generated by the sodium nitrite during coagulation.

Based on the information in the flowsheet, some calculations involving the economics of the project can be made. This is not intended to be detailed but very general to obtain some rough idea about the costs of making starch/rubber masterbatches. Many estimates and assumptions were made. Therefore, these cost calculations should not be taken as absolute.

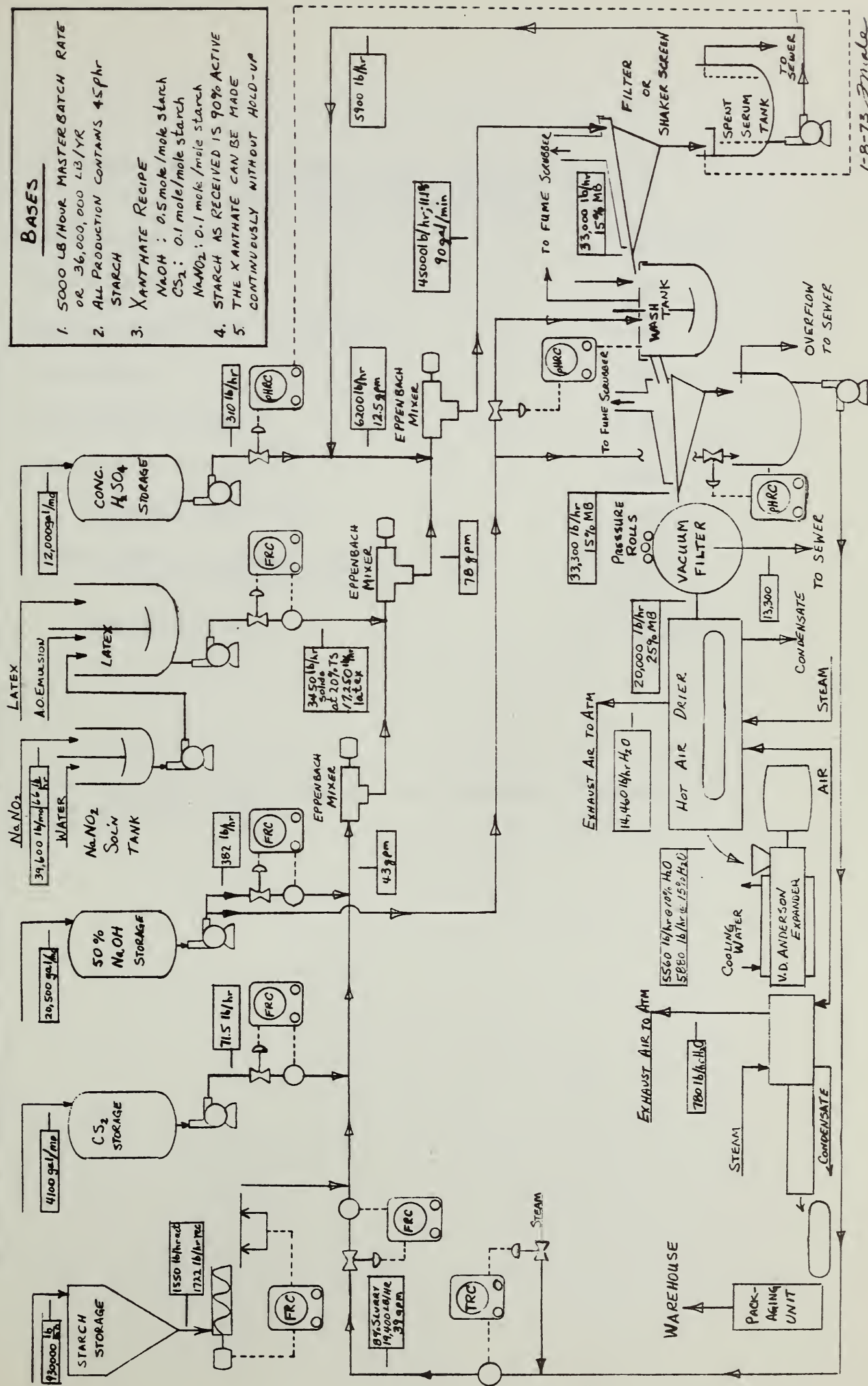
The primary basis for these calculations is that the starch xanthide must carry ALL THE EXTRA costs involved in producing a starch xanthide-rubber masterbatch versus a black pigmented rubber. Thus, in addition to the raw material costs the starch must also bear the costs for handling and storing these materials, the preparation of the xanthate, the higher drying costs associated with the higher water content of starch masterbatches, and extrusion processing.

Table XXII summarizes the various cost estimates for starch xanthide incorporation. The total estimated cost is 9.38 cents per pound. With a minimum of a before Federal Income Tax profit of 12% on the investment, the calculated price is 11.05¢/lb. The calculations are shown as Table XXIII.

The cost of a starch masterbatch may also be calculated. The incorporation cost of carbon black into SBR black masterbatches is 1.2¢/lb. of masterbatch over the raw material costs (rubber at list price for non-pigmented polymer). Since our previous calculations were based on the extra expense of the starch over a black masterbatch, the 1.2¢/lb. should be added in. The cost of a 45 phr starch xanthide/SBR masterbatch would be about 20.5¢/lb.

FIGURE 10

FLOW SHEET FOR A STARCH XANTHIDE / SBR MASTERBATCH PRODUCTION UNIT



1-8-73 P.m.

TABLE XXII - ESTIMATED COST OF STARCH XANTHIDE IN
A 45 PHR SX/SBR MASTERBATCH

Raw Material Costs	6.25¢/lb.
Direct Labor*	0.36
Indirect Labor (80% of Direct)*	0.29
Maintenance*	0.04
Extra Drying Expense*	1.05
Depreciation Allowance*	<u>1.39</u>
Total Estimated Cost	9.38¢/lb.
Profit (12% on investment before Federal Income Tax)	<u>1.67</u>
Estimated Price	11.05¢/lb.

* Over and above that normally associated with production of the synthetic rubber.

TABLE XXIII-CALCULATIONS FOR DETERMINING COST OF INCORPORATING STARCH XANTHIDE IN RUBBER

Raw Materials

<u>Raw Material</u>	<u>Amount</u>	<u>Pound/ hr.</u>	<u>Cents/ lb.</u>	<u>Cents/ hr.</u>
Starch	45 phr	1722	4.0	6888.00
NaOH (50% Caustic)	0.5 mole	382	3.6*	1375.20
Carbon Disulfide	0.1 mole	71.5	4.84*	346.06
Sodium Nitrite	0.1 mole	66	10.65*	702.90
Sulfuric Acid	0.5 mole	240	1.55*	372.00
Total				9684.16

$$\frac{9684.16\text{¢}}{\text{hr.}} \times \frac{1 \text{ hr.}}{1550 \text{ lb. active starch}} = \frac{6.248\text{¢}}{\text{lb. starch in MB}}$$

* Chemical Marketing Reporter; December 18, 1972

Starch Rate

$$\frac{1550 \text{ lb.}}{\text{hr.}} \times \frac{20 \text{ hr.}}{\text{day}} \times \frac{360 \text{ day}}{\text{year}} = 11,300,000 \text{ lb./yr.}$$

Direct Labor

Basis: one extra operator per shift over and above those required for black masterbatch finishing operations to cover following:

raw material handling
sodium nitrite solution preparation
starch xanthate preparation
metering
coagulation
drying
extrusion processing

$$\frac{1 \text{ operator}}{\text{shift}} \times 4 \text{ shifts} \times \frac{\$10,000}{\text{operator/yr.}} \times \frac{1 \text{ year}}{11,300,000 \text{ lb.}} = \frac{\$0.0036}{\text{lb. starch}}$$

Indirect Labor

Basis: 80% of direct labor (Typical)

$$\frac{\$0.0036}{\text{lb. starch}} \times .8 = \frac{\$0.0029}{\text{lb. starch}}$$

Maintenance

Basis: one-half extra man over and above those required for standard rubber finishing operations

$$.5 \text{ operator} \times \frac{\$10,000}{\text{operator/yr.}} \times \frac{1 \text{ Year}}{11,300,000 \text{ lb.}} = \$0.0004$$

TABLE XXIII CONTINUED

Extra Drying Expense

Basis: The dryer feed for a starch masterbatch is 75% water versus 15% water for a normal rubber masterbatch.

$$5,000 \frac{\text{lb. masterbatch}}{\text{hr.}} \times \frac{75 \text{ lb. water}}{25 \text{ lb. dry MB}} = 15,000 \frac{\text{lb. water entering dryer}}{\text{hr.}}$$

$$5,000 \frac{\text{lb. MB}}{\text{hr.}} \times \frac{10 \text{ lb. water}}{90 \text{ lb. MG}} = 550 \frac{\text{lb. water in dryer discharge}}{\text{hr.}}$$

Amount of water to be removed: $15,000 - 550 = 14,450 \text{ lb./hr. water}$

Amount of water normally removed:

$$5,000 \frac{\text{lb. MB}}{\text{hr.}} \times \frac{15 \text{ lb. water}}{85 \text{ lb. MB}} = 880 \frac{\text{lb. water}}{\text{hr.}}$$

Extra water to be removed: $14,450 - 880 = 13,570 \text{ lb/hr. water}$

Extra expense for dryer steam:

$$\frac{13,500 \text{ lb. water}}{\text{hr.}} \times \frac{2 \text{ lb. steam}}{1 \text{ lb. water evap.}} \times \frac{60\text{¢}}{1000 \text{ lb. steam}} \times \frac{1 \text{ HR.}}{1550 \text{ lb. starch}} = \frac{1.05\text{¢}}{\text{lb. starch}}$$

TABLE XXII CONTINUED

Depreciation Allowance

Basis: 10 year straight line depreciation

Capital equals 4 times major equipment cost estimates

Existence of the following equipment is assumed;

caustic storage
sulfuric acid storage
latex storage
shaker screens
wash tank
vacuum filter
hot air dryer
baler

Estimate of major equipment costs:

starch unloading and storage	\$100,000
instrumentation, metering	40,000
tankage	30,000
V.D. Anderson Expander, drive & hood	<u>230,000</u>
Total	\$400,000

Estimated capital: \$400,000 X 4 = \$1,600,000

$$\frac{\$1,600,000}{10 \text{ yr.}} \times \frac{1 \text{ year}}{11,300,000 \text{ lb. starch}} = \$0.0139/\text{lb.}$$

Profit

$$\$1,600,000 \times \frac{.12}{\text{yr.}} \times \frac{1 \text{ year}}{11,300,000 \text{ lb. starch}} = \$0.0167/\text{lb.}$$

NBR

The nitrile/butadiene (NBR) rubbers are specialty polymers in comparison to the general purpose SBR. The NBR market has many variations for specific applications. Even the details of manufacture differ widely between suppliers of NBR. Thus process development of starch/NBR masterbatches must be rather general. The rosin emulsified Hycar 1032 with medium acrylonitrile content was tried first because it was expected to be similar to SBR. Bench scale coagulation studies were also made with another medium acrylonitrile NBR, Hycar 1052, which is emulsified with a linear alkyl sulfonate. The linear alkyl sulfonate (LAS) emulsifiers are not deactivated by acidic conditions as are the fatty and rosin emulsifiers.

Actually the bench scale coagulation conditions for SBR gave a very small crumb which was difficult to handle. Nalco 107, a polyamine coagulation aide, was found to improve the coagulation. The Nalco 107 was premixed with the starch Xanthate solution before the latex was added to prevent any pre-coagulation of the rubber. Nalco 107 concentrations up to 1.5 phr improved the coagulation characteristics. The physical testing data for several samples coagulated by this system are shown in Table XXIV. Air drying the starchxanthide/NBR masterbatches does not give the non-homogeneous cured product that the air dried SBR masterbatches give. The starch and NBR appear to be more compatible than starch and SBR. Extrusion processing, however, will give a softer compound. The addition of resorcinol/formaldehyde results in a harder, shorter compound.

After the poor coagulations obtained for zinc xanthate/SBR masterbatches, it was surprising to find similar masterbatches with Hycar 1032 gave good coagulations. The SX/latex blend was slowly added to the zinc sulfate solution at pH 6-7. Dilute (2%) sulfuric acid was added to the serum to maintain the desired pH. The crumb tended to be fine but the serum drained easily and was clear. The evaluation of several masterbatches prepared by this method is shown in Table XXV. Zinc oxide was not added during compounding since zinc should be available from the zinc starch xanthate. Resorcinol/formaldehyde modification improved the physical properties. Extrusion processing, particularly with the unmodified (no R/F) masterbatches, seems detrimental to the masterbatch properties. These compounds also seemed to have a higher set or slower return rate following elongation. Further work on zinc starch xanthate/NBR masterbatches was dropped because of 1) increased material costs, 2) potential pollution problems, 3) no outstanding property advantage, 4) the apparent need for resorcinol/formaldehyde modification which will color the product.

TABLE XXIV
Evaluation of Starch Xanthide/Hycar 1032 Masterbatches

<u>Sample No.</u>	<u>56P22-3</u>	<u>56P22-4</u>	<u>57P22-5</u>	<u>57P22-5</u>	<u>59P22-10</u>
Starch, phr	30	30	30	45	30
R/F Molar	--	--	.1	--	.2
Coagulation	Cont.	Cont.	Cont.	Cont.	Cont.
Drying	Air	Extruder	Air	Air	Air
Compound No. 36	C	D	E	F	J
<u>Compound Recipe</u>					
Masterbatch	130	130	130	145	130
Zinc Oxide	5	5	5	5	5
Stearic Acid	1	1	1	1	1
Altax	1	1	1	1	1
PBNA	1.25	1.25	1.25	1.25	1.25
Sulfur	1.5	1.5	1.5	1.5	1.5
Cure Time, Mins.	35	35	30	30	35
<u>Physical Properties</u>					
300% Modulus, psi	1350	850	1250	1400	1400
Tensile, psi	1700	1900	1450	1400	1500
Elongation, %	390	500	400	300	350
Durometer A Hard.	73	62	82	83	84

Hycar 1032: Rosin Acid Emulsified Nitrile Rubber
R/F: Resorcinol/Formaldehyde - total moles/mole starch

TABLE XXV
EVALUATION OF 30 PHR ZINC STARCH
XANTHATE/HYCAR 1032 MASTERBATCHES

<u>Masterbatch</u>	<u>89-31-6A</u>	<u>89-31-6E</u>	<u>89-31-7</u>	<u>89-31-7E</u>
Coagulation, ZnSO ₄	4 phr	4 phr	4 phr	4 phr
R/F, mole/mole starch	0.1	0.1	--	
Serum	Tan	Tan	Clear	Clear
Drying	Air	Extruder	Air	Extruder
<u>Compound 913</u>	A	B	C	D
Recipe				
Masterbatch	135	135	135	135
ZnO	--	--	--	--
Stearic Acid	1.0	1.0	1.0	1.0
Sulfur	1.5	1.5	1.5	1.5
MBTS	1.0	1.0	1.0	1.0
PBNA	1.25	1.25	1.25	1.25
<u>Rheometer</u>				
Actual Cure Time, min.	40	50	40	40
<u>Physical Properties, 302°F Cure</u>				
300% Modulus, psi	800	500	450	200
Tensile, psi	1400	1450	1100	400
Elongation, %	580	560	850	670
Hardness, Duro A	64	52	60	50
Tension Set (200% Elongation, hold 1 min. release)				
% Elongation at 5 sec.	150	130	135	130
% Elongation at 1 min.	125	110	115	110

Hycar 1052 is an LAS (linear alkyl sulfonate) emulsified NBR. Normally calcium chloride, aluminum sulfate, or large quantities of sodium chloride are used to coagulate these rubbers. LAS is not acid sensitive. LAS emulsified latex, therefore, requires the development of a separate coagulation system compared with SBR.

Table XXVI describes several Hycar 1052 coagulation experiments. Starch losses are excessive for the calcium chloride and sodium chloride coagulants. Zinc sulfate, far in excess of the 4 to 5 phr ZnO equivalent, gave the best starch retention. Aluminum sulfate may be more practical than zinc sulfate although the starch loss in the serum is higher. The amount of zinc sulfate to give 4 phr ZnO equivalent will not give a complete coagulation. However, the addition of some calcium chloride with the zinc sulfate will give a good coagulation with nearly a clear serum but a fine crumb. Table XXVII indicates that the starch/Hycar 1052 masterbatches have the same deficiencies as the zinc starch xanthate/Hycar 1032 masterbatches. Scale up was not recommended.

TABLE XXVI
COAGULATION OF 30 PHR STARCH/HYCAR 1052 MASTERBATCHES

Sample	Coagulant	phr	% Starch Loss
82P29-1	CaCl_2	10.7	30.0
82P29-2	$\text{Al}_2(\text{SO}_4)_3$	1	6.1
83P29-3	ZnSO_4^*	40.7	3.2
83P29-4	NaCl	62	21.5
83P29-5	NaCl	62	24.9
75P28-6	Nalco 107	--	No coagulation

* Note: ZnSO_4 was added as coagulant without concern to affect on compound

TABLE XXVII

EVALUATION OF STARCH/HYCAR 1052 MASTERBATCHES

<u>Sample No.</u>	<u>82-29-2</u>	<u>82-29-3</u>	<u>78-28-14A</u>	<u>78-28-14B</u>
Coagulation	$\text{Al}_2(\text{SO}_4)_3$	ZnSO_4	ZnSO_4	ZnSO_4
Level, phr	1.0	40.7	CaCl_2	CaCl_2
pH	3.1	6.4	11.8	11.8
Starch Loss, %	6.1	3.2	Clear	----->
Drying	Air	Air	Air	Extruder
Recipe				
Masterbatch	130	-----	-----	----->
Zinc Oxide	5.0	-	-	-
Stearic Acid	1.0	-----	-----	----->
Sulfur	1.5	-----	-----	----->
MBTS	1.0	-----	-----	----->
PBNA	1.25	-----	-----	----->
<u>Rheometer, 3°, 3 cpms, 302°F.</u>				
Max Torque	72	55	47	52
Min. Torque	8.0	4.4	5.2	2.9
Scorch (t_2), Min.	8.7	14.0	5.8	9.0
Optimum Cure (t_{90}), Min.	28	36	10.5	16.5
Cure Time	30	35	10	15
<u>Stress-Strain, Control Recipe, 302°F.</u>				
300% Modulus (psi)	800	350	350	200
Tensile(psi)	1600	1000	1250	400
Elongation (%)	670	900	800	700
Hardness (Duro A)	73	69	68	59

All the pilot plant scale-up coagulations of the NBR masterbatches used the Eppenbach In-Line coagulation process. The two initial coagulations compared no coagulation side versus about 1.0 phr Nalco 107 in the dilute acid. The Nalco 107 did not appear to affect the coagulation. The serum losses, which seemed to be fine crumb or coagulated starch, were about equivalent. These masterbatches were extrusion processed using the V.D.Anderson Expander. The barrel temperature did not increase as rapidly as with the SBR masterbatches. A reduction of the open die area was indicated.

Two 50 pound lots of NBR masterbatches were prepared. Lot G is an air dried 30 phr SX/Hycar 1032 masterbatch. The physical test data for this lot is shown in Table XXVIII. This data indicates that extrusion processing would have been advantageous in preparing this masterbatch.

Lot H is an extrusion processed 30 phr SXRF/Hycar 1032 masterbatch. The resorcinol/formaldehyde level was 0.1 mole/mole starch. In extrusion processing five 1/4-inch round dies were used. The maximum temperature was 330°F; no water was used on the jacket. The Lot H physical testing data (Table XXIX) shows the laboratory processing gives somewhat higher tensile than the Anderson processed material. The modulus for Lot H is higher (better) than Lot G.

TABLE XXVIII- PHYSICAL PROPERTIES OF LOT G (30 PHR SX/HYCAR 1032)

Sample No.	52-15-1	52-15-2	52-15-3	52-16-1	52-16-2	Lot G
Coagulation	Continuous					
Coagulation, pH	1.8	1.8	1.8	1.8	1.8	1.8
Wash pH	Brabender----->					Air
Compound						
Rheometer, 3°, 3 cpms, 302°F.						
Max. Torque	34	32	32.5	26	31	42
Min. Torque	3.0	3.3	2.8	3.4	2.8	5.8
Scorch (t ₂), Min.	14.3	14.0	16.2	19.8	17.4	14.5
Optimum Cure (t ₉₀), Min.	34.5	27.8	37.0	37.7	37.0	32.0
Cure Rate	11.4	16.7	11.0	12.9	11.7	13.2
Stress-Strain, Control Recipe, 302°F.						
300% Modulus	25'	490	480	390	380	690
(psi)	35'	540	530	400	480	800
	50'	660	600	550	510	930
Tensile (psi)	25'	2300	2400	2600	1870	1550
	35'	2620	2530	2080	2350	1700
	50'	2520	2450	2500	2200	1660
Elongation (%)	25'	780	850	940	850	760
	35'	790	800	810	800	700
	50'	730	730	780	700	620
Hardness	25'	58	60	57	56	70
(Duro A)	35'	58	59	59	57	71
	50'	59	60	59	58	72
Specific Gravity	1.113	1.116	1.111	1.101	1.100	1.097

TABLE XXIX - PHYSICAL PROPERTIES OF LOT H (30 PHR SXRF/HYCAR 1032)

Sample No.	P52-13	P52-13-1	P52-13-3	P52-14-1	P52-14-2	P52-14-3	Lot H
Coagulation	Batch	Continuous					
Coagulation, pH	2.0	1.5	1.9	2.2	2.2	2.2	--
Wash pH	4.1	4.0	4.0	4.1	4.1	4.1	--
Drying	Brabender (3 passes)						Anderson
Compound No. 4586	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>7</u>
Rheometer, 3°, 3 cps, 302°F.							
Max. Torque	33	37.5	31	36	32.5	38	30
Min. Torque	3.9	3.2	3.8	3.3	3.7	3.0	3.4
Scorch (t ₂), Min.	20.0	19.0	19.3	19.3	18.5	18.4	10.1
Optimum Cure (t ₉₀), Min.	39.5	42.0	40.0	46.0	37.5	40.0	22.6
Cure Rate	11.8	10.0	11.1	8.6	12.1	10.6	18.4
Stress-Strain, Control Recipe, 302°F.							
300% Modulus	810	700	620	720	700	750	820
(psi)	900	830	840	850	870	940	850
	970	880	890	950	920	970	850
Tensile (psi)	25'	2160	2050	2000	2260	2170	1920
	35'	2080	2080	2080	2000	2250	1780
	50'	2070	2020	2050	2410	2050	1800
Elongation (%)	25'	630	650	620	620	600	540
	35'	540	550	560	520	540	520
	50'	510	510	520	570	480	530
Hardness	25'	61	62	61	61	62	63
(Duro A)	35'	62	62	63	63	62	63
	50'	63	62	62	63	62	63
Specific Gravity	1.113	1.111	1.108	1.110	1.107	1.110	1.107

PRODUCT APPLICATION DEVELOPMENT

Preliminary Accelerator Studies

A preliminary evaluation of accelerator systems for starch xanthide masterbatches was initiated in order to find suitable accelerator systems for applications compounding. The six starch/polymer masterbatches used in the evaluations are shown below:

<u>Lot</u>	<u>Polymer</u>	<u>Starch (phr)</u>	<u>Naphthenic Oil</u>	<u>Resorcinol Formaldehyde (phr)</u>
A	SBR 1503	45	--	--
B	SBR 1708	70	50	-- --
C	SBR 1503	30	--	1.23
D	SBR 1708	55	25	--
G	Hycar 1032	30	--	--
H	Hycar 1032	30	--	1.23

Fourteen accelerators were selected for the study.

<u>Trade Name</u>	<u>Type</u>
Captax	Mercaptobenzothiazole
Altax	Benzothiazyl disulfide
Zenite (10% wax)	Zinc mercaptolbenzothiazole
Santocure	Benzothiazolsulfenamide
Ethylac	Benzothiazyl thio carbamyl sulfide
Butyl Zimate	Zinc dithiocarbamate
Bismate	Bismuth dithiocarbamate
Unads	Thiuram monosulfide
Methyl Tuads	Thiuram disulfide
Beutene	Aldehyde-amine reaction product
DBA	Mixed amines
DOTG	Guanidine
Thiate E	Thiourea
ZBX	Zinc xanthate

Some of these materials were included because they may be used as secondary accelerators in future work.

In our procedure we masterbatched each of the six elastomers in a laboratory Banbury using the following recipe:

Elastomer	Variable (to give 100 parts polymer)
Zinc Oxide	5.0
Stearic Acid	2.0
PBNA	1.25

These masterbatches were divided into mill-batch-sized portions and the sulfur (2 phr) and accelerators were added on a lab mill. We used three accelerator levels (0.625, 1.25 and 2.5 phr) for each accelerator. The mixed stocks were tested for cure characteristics (Monsanto Rheometer @300°F). Using the optimum cures (t_{90}), samples were cured and tested for stress-strain properties and Shore A2 hardness.

The results of the tests for the six starch/elastomer masterbatches are shown in Tables XXX through XXXV. This basic information was used in designing compounds for specific applications.

Compound Development

Based on the extensive preliminary accelerator study, the optimum accelerators and levels were selected for each starch/elastomer MB. One optimum recipe for each starch/elastomer masterbatch was submitted to the laboratory for extensive processing and physical testing evaluations. The masterbatches used in the recipes are shown below.

<u>Lot</u>	<u>Base Polymer</u>	<u>SX, phr</u>	<u>Oil, phr</u>	<u>RF, phr</u>
Lot A	SBR 1503	45	--	--
Lot B2	SBR 1708	70	50	--
Lot C	SBR 1503	30	--	1.23
Lot D2	SBR 1708	55	25	--
Lot G	Hycar 1032	30	--	--
Lot H	Hycar 1032	30	--	1.23

The recipes and test data are shown in Table XXXVI.

The results of the evaluation indicate that the nitrile/starch masterbatches yield superior physical properties compared to the SBR/starch masterbatches. They also show the excellent oil resistance and hot air aging typical of nitrile polymers.

Other than poor flex resistance, short elongation and poor water resistance the other physical properties of both the SBR and nitrile/starch masterbatches are in an acceptable range for many rubber products. In fact, the modulus, hardness and abrasion resistance values are higher than would be expected for stocks with low loadings of a reinforcing filler.

The stocks in Tables XXXVII and XXXVIII were developed in order to show a comparison of the starch masterbatches with SBR and Hycar stocks containing nonblack fillers. The starch masterbatches yield reinforcing intermediate between HiSil and Silene D. It is interesting to note the high modulus and hardness values of the starch masterbatch stocks. Stocks with only 30 phr of starch yield modulus and hardness values in line with stocks containing 75 phr of Silene D.'

The substitution of starch masterbatch Lot C for 1833-G1 in a typical tread rubber compound is shown in Table XXXIX. The substitution at the 25 and 50 percent level did not drastically change the physical properties of the control stock. Of interest is the lower heat build-up obtained on the blends and the similar abrasion resistance. All of the properties are in the acceptable range for tread rubber.

TABLE XXX - ACCELERATOR STUDY FOR LOT A MASTERBATCH (45 PHR SX/SBR 1503)

Monsanto Rheometer

(3°Arc, 3 cpm, 300°F.)

Recipe Number	Accelerator	phr	Scorch			Opt. Cure	100K	Stress-Strain Properties			
			Max. Torque	Min. Torque	Time			Tensile Strength	Elong.	300% Mod.	Shore A2 Hard.
1	Captax	.625		6.3	9.2	76.0	3.5	1290	300	1290	58
2		1.25	72.5	6.9	7.2	49.3	5.2	1330	270	--	59
3		2.5	75.7	7.0	5.8	36.2	7.6	1240	250	--	59
4	Altax	.625	84.4	5.7	14.7	131.0	2.0	--	--	--	--
5		1.25	80.8	5.5	15.8	93.8	2.9	1520	350	1300	58
6		2.5	78.9	5.2	16.6	70.1	4.3	1730	360	1430	60
7	Zenite*	.69	67.6	6.1	9.4	102.8	2.5	2010	480	1210	60
8		1.39	72.4	6.1	7.9	70.5	3.7	1890	430	1250	62
9		2.78	74.2	6.0	6.9	53.8	4.9	2020	390	1420	60
10	Santocure	.625	70.4	6.0	15.0	57.0	5.5	2050	450	1260	62
11		+1.25	76.6	6.0	16.0	32.4	14.0	1600	320	1430	60
12		+2.5	85.2	5.1	15.7	24.7	25.6	1350	270	--	63
13	Ethylac	.625	--	-6.7	23.5	--	--	--	--	--	--
14		1.25	193.0	6.7	22.5	224.7	1.1	--	--	--	--
15		2.5	78.6	6.0	19.0	50.6	7.3	1540	260	--	64
16	Butyl Zimate	.625	72.0	6.4	8.7	43.7	6.6	1700	380	1160	60
17		1.25	77.0	6.6	7.2	41.1	6.8	1240	280	--	63
18		2.5	88.9	7.1	5.6	35.6	7.7	1150	240	--	63
19	Bismate	+ .625	97.3	7.1	3.2	10.3	32.4	2250	320	2170	66
			(91.4)	(7.1)	(3.7)	(11.1)	(31.1)				
20		+1.25	85.1	6.6	3.6	10.9	31.5	1920	280	--	65
			(94.1)	(7.6)	(3.1)	(10.4)	(31.5)				
21		+2.5	86.1	6.8	3.7	11.3	30.3	2340	270	--	66
			(97.6)	(8.3)	(3.5)	(12.4)	(25.8)				
22	Unads	+ .625	83.8	6.0	9.8	17.8	28.8	1710	360	1320	61
23		+1.25	91.5	5.3	10.2	20.6	22.1	970	190	--	65
24		+2.5	99.7	6.8	8.8	16.3	30.7	1120	200	--	65

* 10% wax. Adjusted to give .625, 1.25, & 2.5 phr Zenite Special. ** Did not cure.
Values in parentheses are retests.

TABLE XXX CONTD.--ACCELERATOR STUDY FOR LOT A MASTERBATCH (45 PHR SX/SBR 1503)

Monsanto Rheometer

(3° Arc, 3 cpm, 300°F.)

Recipe Number	Accelerator	phr	Min.			Scorch Opt.		Stress-Strain Properties			
			Max.	Torque	Torque	Time	Cure	Tensile Strength	Elong.	300% Mod.	Shore A2 Hard.
25	Methyl Tuads	+ .625	90.2	6.3	5.2	15.3	22.8	1310	300	1310	62
26		+1.25	98.1	5.8	5.2	15.7	21.9	990	140	--	65
27		+2.5	101.9	8.8	4.0	9.4	42.6	1300	170	--	67
28	Bentene	.625	70.5	5.4	12.0	163.3	1.5	1710	410	1080	57
29		1.25	58.9	5.8	6.9	48.7	5.5	1510	400	980	57
30		2.5	51.8	4.2	6.5	49.0	5.4	--	--	--	--
31	DBA	.625**	--	--	--	--	--	--	--	--	--
32		1.25**	--	--	--	--	--	--	--	--	--
33		2.5**	--	--	--	--	--	--	--	--	--
34	DOTG	.625**	--	--	--	--	--	--	--	--	--
35		1.25**	--	--	--	--	--	--	--	--	--
36		2.5	67.9	5.9	7.7	118.7	2.1	--	--	--	--
37	Thiate E	.625**	--	--	--	--	--	--	--	--	--
38		1.25**	--	--	--	--	--	--	--	--	--
39		2.5**	113.4	5.7	7.1	330.9	0.7	--	--	--	--
40	ZBX	.625**	--	--	--	--	--	--	--	--	--
41		1.25**	--	--	--	--	--	--	--	--	--
42		2.5**	--	--	--	--	--	--	--	--	--

** Did not cure.

TABLE XXXI- ACCELERATOR STUDY FOR LOT B MASTERBATCH (70 SX/50 NAPHTHENIC OIL/SBR 1708)

Monsanto Rheometer

(3° Arc, 3 cpm, 300°F.)

Recipe Number	Accelerator	phr	Max. Min. Scorch			Opt. Cure	Stress-Strain Properties			
			Torque	Torque	Time		Tensile Strength	Elong.	300% Mod.	Shore A2 Hard.
43	Captax	.625	64.6	5.0	12.3	179.6	---	---	---	---
44		1.25	48.3	3.4	11.8	87.7	1160	310	1070	55
45		2.5	57.9	5.0	9.4	54.2	1240	370	1110	57
46	Altax	.625**	---	---	---	---	---	---	---	---
47		1.25	116.7	4.3	21.0	265.5	---	---	---	---
48		2.5	72.6	3.0	24.8	134.9	1210	330	1120	57
49	Zenite*	.69	106.0	5.2	14.4	365.7	---	---	---	---
50		1.39	52.1	3.3	12.5	108.9	1350	500	1010	57
51		2.78	58.6	4.3	9.0	54.8	1310	410	1060	57
52	Santocure	.625**	70.4	3.3	19.5	159.7	---	---	---	---
53		+1.25	61.0	5.5	16.2	38.0	1450	450	1050	56
54		+2.5	63.6	3.0	18.5	30.0	1290	320	1190	59
55	Ethylac	.625	74.1	6.2	18.1	110.4	1230	430	980	57
56		1.25	60.1	3.2	19.3	58.0	1270	370	1140	59
57		2.5	74.0	5.5	13.6	32.1	1270	300	1270	57
58	Butyl Zimate	.625	47.9	3.3	8.8	39.0	1300	470	1030	56
59		1.25	53.6	3.8	7.8	31.8	1220	400	1060	56
60		2.5	62.2	3.7	6.1	28.4	1260	350	1170	58
61	Bismate	+ .625	59.3	4.3	4.8	14.3	1500	370	1300	60
62		+1.25	69.9	4.6	5.1	13.8	1380	270	---	61
63		+2.5	72.1	5.5	3.9	12.9	1390	270	---	62
64	Unads	+ .625	63.2	6.2	12.0	23.2	1340	400	1140	58
65		+1.25	67.4	3.2	13.2	25.7	1240	280	---	60
66		+2.5	78.9	4.0	10.3	20.4	1190	200	---	64

* 10% wax. Adjusted to give .625, 1.25, & 2.5 phr Zenite Special. ** Did not cure.

TABLE XXXI- ACCELERATOR STUDY FOR LOT B MASTERBATCH (CONT.)

Recipe Number	Accelerator	phr	Monsanto Rheometer (3° Arc, 3 cpm, 300°F.)				Stress-Strain Properties				
			Max. Torque	Min. Torque	Scorch Time	Opt. Cure	100K	Tensile Strength	Elong.	300% Mod.	Shore A2 Hard.
67	Methyl Tuads	+ .625	64.0	5.0	6.2	17.8	19.8	1310	340	1190	59
68		+1.25	69.3	3.8	6.1	16.9	21.3	1270	230	--	61
69		+2.5	83.9	4.2	4.9	13.8	25.8	1280	190	--	67
70	Bentene	.625**	--	--	--	--	--	--	--	--	--
71		1.25	40.1	5.3	11.8	104.9	2.5	1300	500	930	55
72		2.5	39.1	4.2	6.5	50.3	5.2	1230	520	860	54
73	DBA	.625**	--	--	--	--	--	--	--	--	--
74		1.25**	--	--	--	--	--	--	--	--	--
75		2.5**	--	--	--	--	--	--	--	--	--
76	DOTG	.625**	--	--	--	--	--	--	--	--	--
77		1.25**	--	--	--	--	--	--	--	--	--
78		2.5**	--	--	--	--	--	--	--	--	--
79	Thiate E	.625**	--	--	--	--	--	--	--	--	--
80		1.25**	--	--	--	--	--	--	--	--	--
81		2.5**	--	--	--	--	--	--	--	--	--
82	ZBX	.625**	--	--	--	--	--	--	--	--	--
83		1.25**	--	--	--	--	--	--	--	--	--
84		2.5**	--	--	--	--	--	--	--	--	--

** Did not cure.

TABLE XXXII-ACCELERATOR STUDY FOR MASTERBATCH LOT C (30 PHR SXRF/SBR 1503)

Recipe Number	Accelerator	phr	Monsanto Rheometer (3° Arc, 3 cpm, 300°F.)			Scorch Time	Opt. Cure	100K	Stress-Strain Properties		
			Max. Torque	Min. Torque	Max. Torque				Tensile Strength	300% Elong. Mod.	Shore A2 Hard.
85	Captax	.625**	--	--	--	--	--	--	--	--	--
86		1.25	132.2	8.3	13.7	331.5	.72		--	--	--
87		2.5	90.6	5.4	12.7	201.8	1.21		--	--	--
88	Altax	.625**	--	--	--	--	--	--	--	--	--
89		1.25	84.9	5.3	21.9	211.6	1.21		--	--	--
90		2.5	73.2	9.7	19.7	68.6	4.7		1240	330	58
91	Zenite*	.69	140.9	8.0	13.4	359.1	0.67		--	--	--
92		1.39	133.5	9.1	11.9	310.5	0.77		--	--	--
93		2.78**	--	--	--	--	--	--	--	--	--
94	Santocure	.625	80.5	6.7	16.8	102.5	2.7		1430	350	62
95		1.25	81.4	6.0	16.8	41.5	9.3		1710	340	62
96		+2.5	87.8	5.8	13.8	24.2	22.1		1340	250	63
97	Ethylac	+ .625	78.1	7.2	15.1	42.6	8.4		1240	290	62
98		+1.25	80.6	6.9	14.1	37.0	10.0		1640	330	61
99		2.5	97.0	6.0	12.6	34.1	10.7		1360	230	63
100	Butyl Zimate	.625	66.8	6.7	8.1	41.5	6.9		1290	300	60
101		1.25	82.5	8.0	6.2	29.2	10.0		1390	240	62
102		2.5	88.1	6.5	5.2	27.8	10.2		1170	220	64
103	Bismate	+ .625	80.9	7.3	2.8	10.9	28.4		1790	320	63
104		+1.25	100.0	8.6	2.7	12.2	24.2		1850	260	65
105		+2.5	91.3	7.6	2.8	11.2	27.4		1680	260	65
106	Unads	.625	76.1	6.4	9.2	24.1	15.5		1920	300	62
107		+1.25	94.1	6.4	8.6	18.8	22.5		1270	220	65
108		+2.5	100.0	6.1	8.2	18.5	22.3		1200	160	65
109	Methyl Tuads	+ .625	78.6	6.8	5.2	20.4	15.1		1630	280	62
110		+1.25	100.0	7.0	4.3	14.2	23.2		1420	220	65
111		+2.5	93.3	6.5	3.7	10.9	31.9		1230	150	70
112	Bentene	.625**	--	--	--	--	--	--	--	--	--
113		1.25**	--	--	--	--	--	--	--	--	--
114		2.5	53.2	5.9	7.8	52.9	5.1		420	630	280

TABLE XXXII CONTD-ACCELERATOR STUDY FOR MASTERBATCH LOT C (30 PHR SXRF/SBR 1503)

Monsanto Rheometer

(3° Arc, 3 cpm, 300°F.)

Recipe Number	Accelerator	phr	Max. Torque			Scorch Opt.		100K	Stress-Strain Properties			
			Max. Torque	Min. Torque	Time	Cure	Opt. Cure		Tensile Strength	Elong. Mod.	300% Shore	A2 Hard.
115	DBA	.625**	--	--	--	--	--	--	--	--	--	--
116		1.25**	--	--	--	--	--	--	--	--	--	--
117		2.5**	--	--	--	--	--	--	--	--	--	--
118	DOTG	.625**	--	--	--	--	--	--	--	--	--	--
119		1.25**	--	--	--	--	--	--	--	--	--	--
120		2.5	98.0	6.2	8.3	205.2	1.2	1.2	--	--	--	--
121	Thiate E	.625**	--	--	--	--	--	--	--	--	--	--
122		1.25**	--	--	--	--	--	--	--	--	--	--
123		2.5	82.6	5.6	10.0	396.5	0.60	0.60	--	--	--	--
124	ZBX	.625**	--	--	--	--	--	--	--	--	--	--
125		1.25**	--	--	--	--	--	--	--	--	--	--
126		2.5**	--	--	--	--	--	--	--	--	--	--

** Did not cure.

TABLE XXXIII-ACCELERATOR STUDY FOR MASTERBATCH LOT D (55 SX/25 NAPHTHENIC OIL/SBR 1708)

Recipe Number	Accelerator	phr	Monsanto Rheometer (3° Arc, 3 cpm, 300°F.)				Stress-Strain Properties			
			Max. Torque	Min. Torque	Scorch Opt.		Tensile Strength	300% Mod.		Shore A2 Hard.
					Time	Cure		Elong.	Mod.	
127	Captax	.625**	65.2	7.0	11.6	140.7	--	--	--	--
128		1.25	67.0	6.2	9.6	96.2	1420	320	1410	61
129		2.5	66.1	6.8	7.3	55.1	1390	300	1390	62
130	Altax	.625**	150.2	5.7	18.9	440.1	--	--	--	--
131		1.25**	90.8	6.8	16.6	155.2	--	--	--	--
132		2.5	71.3	5.7	19.6	84.6	1630	480	1430	62
133	Zenite*	.69**	61.7	7.8	11.2	126.6	--	--	--	--
134		1.39	64.6	6.2	10.1	95.1	1610	440	1220	60
135		2.78	67.0	7.2	12.2	47.8	1720	470	1280	59
136	Santocure	.625	72.2	6.8	16.3	100.1	1410	400	1110	59
137		+1.25	69.2	7.1	15.2	34.8	1390	370	1260	61
138		2.5	78.1	6.0	17.1	28.9	1390	320	1300	61
139	Ethylac	.625	73.8	8.1	16.4	73.8	1510	430	1160	61
140		1.25	68.6	6.3	13.0	42.0	1580	400	1310	62
141		2.5	83.6	6.1	13.0	36.0	1370	280	--	63
142	Butyl Zimate	.625	58.4	7.0	7.3	34.4	1550	460	1180	60
143		1.25	61.9	10.3	7.2	36.9	1470	400	1270	62
144		2.5	73.1	6.9	5.1	29.7	1340	230	--	62
145	Bismate	.625	72.3	7.9	3.6	12.3	1750	310	1610	64
146		1.25	88.0	8.6	3.6	12.8	1450	220	--	66
147		2.5	83.0	7.5	3.6	13.8	1570	240	--	65
148	Unads	.625	71.7	7.0	10.0	21.0	1580	400	1350	65
149		1.25	75.4	8.4	11.0	21.9	1350	300	1350	64
150		2.5	91.5	5.8	10.3	21.0	1180	180	--	70

* 10% wax. Adjusted to give .625, 1.25, & 2.5 phr Zenite Special. ** Did not cure.

TABLE XXXIII- ACCELERATOR STUDY FOR MASTERBATCH LOT D (55 SX/25 NAPHTHENIC OIL/SBR 1708 CONT'D.)

Recipe Number	Accelerator	phr	Monsanto Rheometer (3° Arc, 3 cpm, 300°F.)					Stress-Strain Properties			
			Torque	Torque	Cure	Time	100K	Tensile Strength	Elong.	300% Mod.	Shore A2 Hard.
151	Methyl Tuads	.625	73.7	6.9	16.2	5.8	22.1	1540	240	--	64
152		1.25	87.4	7.7	14.2	4.9	24.7	1440	240	--	67
153		2.5	100.0	6.6	14.2	4.6	24.0	1290	170	--	71
154	Bentene	.625**	--	--	--	--	--	--	--	--	--
155		1.25	53.8	7.2	85.4	10.0	3.1	1570	420	1110	60
156		2.5	48.6	6.2	47.0	6.7	5.7	1360	400	1110	59
157	DBA	.625**	--	--	--	--	--	--	--	--	--
158		1.25**	--	--	--	--	--	--	--	--	--
159		2.5**	--	--	--	--	--	--	--	--	--
160	DOTG	.625**	--	--	--	--	--	--	--	--	--
161		1.25**	--	--	--	--	--	--	--	--	--
162		2.5**	75.4	7.0	210.4	10.3	1.1	--	--	--	--
163	Thiate E	.625**	--	--	--	--	--	--	--	--	--
164		1.25**	--	--	--	--	--	--	--	--	--
165		2.5**	120.6	6.5	749.8	11.2	0.31	--	--	--	--
166	ZBX	.625**	--	--	--	--	--	--	--	--	--
167		1.25**	--	--	--	--	--	--	--	--	--
168		2.5**	--	--	--	--	--	--	--	--	--

** Did not cure.

Monsanto Rheometer (3° Arc, 3 cpm, 310°F)												
Recipe Number	Accelerator	phr -	Max.		Min. Torque	Scorch		Opt. Cure	100K	Stress-Strain Properties		
			Torque	Torque		Time				Tensile Strength	Elong.	300% Mod.
169	Captax	.625	53.9	4.2	5.2	48.4	5.3	2010	610	1010	67	
170		1.25	58.7	5.0	6.5	23.7	10.0	1970	590	960	65	
171		2.5	57.1	5.0	4.7	16.2	20.0	2000	580	970	64	
172	Altax	.625	41.1	4.7	16.6	53.5	6.2	1940	610	990	64	
173		1.25	55.8	4.1	16.1	46.6	7.5	1920	510	1090	66	
174		2.5	52.9	4.2	15.2	27.4	18.9	2150	510	1200	65	
175	Zenite*	.69	51.4	4.5	9.6	60.9	4.5	2210	650	920	65	
176		1.39	52.9	5.5	6.8	25.4	12.4	2190	630	970	65	
177		2.78	57.0	4.7	6.3	21.0	15.6	2080	580	990	63	
178	Santocure	.625	40.7	4.2	14.6	41.7	8.5	2170	580	1040	66	
179		1.25	61.1	4.6	13.7	35.7	10.5	1990	480	1230	69	
180		2.5	58.0	4.0	12.5	18.3	39.7	1890	450	1300	67	
181	Ethylac	.625	67.2	5.0	12.8	21.8	25.6	2210	500	1290	69	
182		1.25	66.3	5.0	10.5	15.1	50.0	2200	440	1460	71	
183		2.5	77.4	5.0	9.3	14.1	47.9	1900	360	1560	69	
184	Butyl Zimate	.625	68.8	5.1	5.1	11.8	34.3	2040	500	1190	67	
185		1.25	76.2	6.0	4.5	23.0	12.4	1920	390	1470	70	
186		2.5	78.8	7.3	4.1	19.6	14.9	1880	370	1540	69	
187	Bismate	.625	76.8	6.8	2.6	11.3	26.4	1820	390	1490	72	
188		1.25	88.1	6.7	2.6	12.2	24.0	1780	290	---	74	
189		2.5	93.1	6.0	3.3	10.6	31.5	1910	280	---	75	
190	Unads	.625	62.0	4.2	11.5	15.7	54.8	1910	400	1440	69	
191		1.25	80.0	5.0	11.7	14.3	88.5	1870	330	1690	73	
192		2.5	76.2	4.1	11.3	16.2	46.9	1850	310	1730	71	

* 10% wax. Adjusted to give .625, 1.25, + 2.5 Zenite Special.

TABLE XXXIV LOT G ACCELERATION SYSTEM (CONT.)

Recipe Number	Accelerator	Monsanto Rheometer (3° Arc, 3 cpm, 310°F)							Stress-Strain Properties			
		phr	Max.		Min. Torque	Scorch Opt.		100K	Tensile Strength	300% Elong. Mod.	Shore A2 Hard.	
			Torque	Torque		Time	Cure					
193	Methyl Tuads	.625	76.4	4.6	7.1	11.0	39.0	1870	370	1500	68	
194		1.25	81.8	4.2	5.9	9.6	62.2	1770	300	1730	67	
195		2.5	99.0	4.9	5.4	9.6	54.8	1970	280	--	69	
196	Beutene	.625**	88.5	3.6	9.7	230.6	1.0	--	--	--	--	
197		1.25	58.9	5.0	7.4	67.2	3.8	1810	480	1130	65	
198		2.5	64.9	5.1	6.3	29.6	9.9	1980	560	1020	64	
199	DBA	.625**	--	--	--	--	--	--	--	--	--	
200		1.25**	--	--	--	--	--	--	--	--	--	
201		2.5**	--	--	--	--	--	--	--	--	--	
202	DOTG	.625**	150.8	4.8	10.6	441.2	.5	--	--	--	--	
203		1.25	67.9	3.1	7.6	105.9	2.3	1950	420	1340	67	
204		2.5	74.1	5.0	5.5	53.3	4.8	2170	480	1270	66	
205	Thiate E	.625**	--	--	--	--	--	--	--	--	--	
206		1.25**	--	--	--	--	--	--	--	--	--	
207		2.5**	148.4	3.3	9.1	370.5	0.6	--	--	--	--	
208	ZBX	.625**	--	--	--	--	--	--	--	--	--	
209		1.25**	--	--	--	--	--	--	--	--	--	
210		2.5**	--	--	--	--	--	--	--	--	--	

** Did not cure.



TABLE XXXV - LOT H ACCELERATION SYSTEM

Monsanto Rheometer (3° Arc, 3 cpm, 310°F)										Stress-Strain Properties			
Recipe Number	Accelerator	phr	Max.		Min. Torque	Scorch Opt.		100K	Tensile		300% Mod.	Shore A2 Hard.	
			Torque			Time	Cure		Strength	Elong.			
211	Captax	.625	44.6		4.2	9.0	34.6	9.0	1600	330	1370	63	
212		1.25	56.5		4.0	7.0	29.9	10.0	2310	430	1510	65	
213		2.5	62.6		5.1	4.5	16.9	18.5	2090	400	1450	62	
214	Altax	.625***	112.8		3.2	17.2	232.3	1.1	2200	480	1290	69	
215		1.25	44.4		4.1	17.5	41.3	9.6	2200	440	30	69	
216		2.5	61.9		3.2	16.2	35.4	12.0	2130	390	1510	67	
217	Zenite*	.625	44.0		4.3	9.9	48.6	5.9	2170	520	1130	66	
218		1.39	54.8		3.9	7.8	36.5	8.0	2290	450	1350	67	
219		2.78	60.2		4.3	6.3	20.5	16.2	1210	780	540	66	
220	Santocure	.625	58.6		3.3	14.2	64.1	4.6	2360	480	1400	70	
221		1.25	29.0		4.0	16.8	65.5	4.7	2320	470	1350	67	
222		2.5	52.9		3.8	11.6	19.2	30.3	1940	350	1600	70	
223	Ethylac	.625	55.0		4.0	13.0	20.4	31.1	2220	400	1590	67	
224		1.25	71.0		4.1	9.5	14.7	44.2	1770	350	1380	64	
225		2.5	73.7		3.8	10.1	14.2	56.1	1970	310	1880	65	
226	Butyl Zimate	.625	77.2		4.9	5.0	12.2	31.9	2270	380	1760	71	
227		1.25	68.0		4.9	4.1	9.4	43.4	1340	490	1370	68	
228		2.5	83.6		4.8	3.8	7.5	62.2	1890	290	--	71	
229	Bismate	.625	80.0		5.8	3.1	8.7	41.1	1860	280	--	68	
230		1.25	96.8		6.3	2.4	8.7	36.5	1720	230	--	74	
231		2.5	103.0		6.2	2.7	9.9	31.9	1950	230	--	70	
232	Unads	.625	69.2		3.3	11.8	15.3	65.7	1990	300	1990	68	
233		1.25	59.8		3.0	12.0	15.3	69.7	2000	270	--	68	
234		2.5	78.2		3.0	10.7	14.4	62.2	2070	260	--	69	

* 10% wax. Adjusted to give .625, 1.25, + 2.5 Zenite Special. *** 60 min. cure used.

TABLE XXXV-LOT H ACCELERATION SYSTEM (CONT.)

Recipe Number	Accelerator	Monsanto Rheometer (3° Arc, 3 cpm, 310°F)					Stress-Strain Properties				
		phr	Max. Torque	Min. Torque	Scorch Time	Opt. Cure	100K	Tensile Strength	Elong.	300% Mod.	Shore A2 Hard.
235	Methyl Tuads	.625	78.7	3.7	6.2	9.7	38.3	1960	280	--	70
236		1.25	87.6	3.6	5.7	9.3	40.4	2120	270	--	72
237		2.5	102.1	3.6	4.6	8.1	51.1	1800	190	--	73
238	Beutene	.625**	104.7	4.0	11.6	364.7	0.7	--	--	--	--
239		1.25	39.4	3.8	9.1	54.4	5.1	2360	430	1410	65
240		2.5	62.4	4.2	7.1	50.4	5.3	2340	420	1540	67
241	DBA	.625**	--	--	--	--	--	--	--	--	--
242		1.25**	--	--	--	--	--	--	--	--	--
243		2.5**	--	--	--	--	--	--	--	--	--
244	DOTG	.625**	222.2	4.0	11.1	636.3	0.4	--	--	--	--
245		1.25	75.2	4.0	6.9	82.9	3.0	2030	470	1180	67
246		2.5	79.1	4.2	6.1	55.3	4.7	2450	400	1790	69
247	Thiate E	.625**	--	--	--	--	--	--	--	--	--
248		1.25**	--	--	--	--	--	--	--	--	--
249		2.5**	98.1	4.3	9.3	194.4	1.2	--	--	--	--
250	ZBX	.625**	--	--	--	--	--	--	--	--	--
251		1.25**	--	--	--	--	--	--	--	--	--
252		2.5**	--	--	--	--	--	--	--	--	--

** Did not cure.

TABLE XXXVI

<u>Recipe</u>	<u>1</u>	<u>2A</u>	<u>3</u>	<u>4A</u>	<u>5</u>	<u>6B</u>
<u>Polymer Identification</u>	Lot A	Lot B2	Lot C	Lot D2	Lot G	Lot H
<u>Ingredients, phr</u>						
Lot A	145.00	--	--	--	--	--
Lot B2	--	220.00	--	--	--	--
Lot C	--	--	131.23	--	--	--
Lot D2	--	--	--	180.00	--	--
Lot G	--	--	--	--	130.00	--
Lot H	--	--	--	--	--	131.2
Zinc Oxide	5.00	5.00	5.00	5.00	5.00	5.00
Stearic Acid	2.00	2.00	2.00	2.00	2.00	2.00
PBNA	1.25	1.25	1.25	1.25	1.25	1.25
Bismate	0.5	--	--	--	--	0.625
Unads	--	--	0.625	--	--	--
Ethylac	--	1.25	--	1.25	0.625	--
Sulfur	2.00	2.00	2.00	2.00	2.00	2.00
Total	155.75	231.50	142.105	191.50	140.875	142.10

COMPOUND PROCESSING PROPERTIES

Compound Mooney, ML-4, 212°F	72	52	74	77	84	76
<u>Mooney Scorch, ML, 266°F</u>						
Minutes to 5 pt. rise	5.3	30+	16.1	30+	24.3	4.0
Minutes to 35 pt. rise	9.7	-1	21.5	--	30+	7.2
Index	4.4	--	5.4	--	--	3.2

 Monsanto Rheometer

(3° arc, 3 cpm, 300°F)						
Maximum Torque	85.3	63.2	100.2	78.9	76.2	73.1
Minimum Torque	9.8	4.7	7.9	8.1	6.1	7.2
Scorch Time (t ₂), Minutes	4.2	17.4	8.8	14.8	14.1	2.9
Optimum Cure (t ₉₀), Minutes	11.5	59.4	16.8	50.5	24.9	12.5
Cure Rate (k) X 100	31.5	5.5	28.8	6.4	21.3	24.0

Green Strength

Yield Strength, psi	101	--	88	--	141	126
Yield Elongation, %	200	--	60	--	50	50
Ultimate Strength, psi	75	--	33	--	8	8
Ultimate Elongation, %	400	--	310	--	1450	640

Tel-Tac

Tack, psi	16.7	--	21.0	--	38.2	36.2
Stickiness, psi	4.2	--	5.3	--	8.7	7.0

UNAGED VULCANIZATE PROPERTIES

<u>Stress-Strain</u>	*		*		*		*		*	
Tensile Strength, psi	8	2200		-- 14	1640		-- 21	1980	6	2010
	12	2090	60	1270	17	1680	45	1580	25	1860
	25	1950		-- 30	990		-- 40	1810	30	1850
Elongation, %	8	380		-- 14	320		-- 21	500	6	330
	12	340	60	370	17	300	45	400	25	470
	25	300		-- 30	200		-- 40	440	30	300

* Min. Cured @300°F

TABLE XXXVI CONTD.

<u>Recipe</u>	<u>1</u>	<u>2A</u>	<u>3</u>	<u>4A</u>	<u>5</u>	<u>6B</u>
<u>UNAGED VULCANIZATE PROPERTIES CON'T.</u>						
<u>Stress-Strain</u>	*	*	*	*	*	*
300% Modulus, psi	8 1700	-- 14 1510	-- 21 1200	6 1790	12 1870	60 1140
	12 1870	60 1140	17 1680	45 1310	25 1210	13 1900
	25 1950	-- --	-- --	40 1210	30 1210	30 1850
Shore A2 Hardness	8 64	-- 14 65	-- 21 71	6 70	12 64	60 59
	12 64	60 59	17 65	45 62	25 72	13 72
	25 64	-- 20 67	-- 40 72	30 69		
Angle Tear Resistance, ppi	8 168	-- 14 132	-- 21 232	6 210	12 168	-- 17 125
Die C, Pulled w/grain	12 168	-- 17 125	-- 25 218	13 192	25 150	-- 30 112
	25 150	-- 30 112	-- 40 225	30 175		
<u>Optimum Cure Time @300°F</u>	<u>12</u>	<u>60</u>	<u>17</u>	<u>51</u>	<u>25</u>	<u>13</u>
<u>Goodrich Flex</u>						
(.175" stroke, 55 lbs. load, 212°F)						
(opt. cure + 15 min.)						
Initial Static Compression	.146	.206	.145	.185	--	--
Initial Dynamic Compression	.056	.120	.056	.0945	--	--
at T, °F	28	36.5	24	40	--	--
Permanent Set, %	6.5	4.46	4.8	Ex. Blow-Outs	--	--
Compression Set, %	36.8	28.97	30.28	26.32	26.17	25.84
(Method B, 72 hrs., 158°F)	--	27.52	--	25.66	--	--
(Opt. cure + 8 min.)						
<u>Skid Resistance, British Portable</u>						
(Opt. cure + 4 min.)						
Glass, dry	88	88.8	98	93.8	93	78
, wet	52	37.0	53	43.6	59	59
Pico Abrasion Index	66	39	80	46	97	96
(Opt. cure + 8 min.)						
NBS Abrasion Resistance,	234	87	314**	101	165	287**
Per Cent of Standard						
DeMattia Flex, Flexures	600***	1200	10***	600	20***	600***
to 0.6" crack growth, 212°F	--					
(Opt. cure + 4 min.)						
Ross Flex (Aged 24 hrs. @212°F) R.T.	110,576	206,488/.4"	--	160,526/.6	--	59,434
Belt Flex (Time to failure (hrs.))	24	--	--	--	--	24

* Estimated, too high for exact measurement

** Broke immediately

*** Recompounded

TABLE XXXVI CONTD.

<u>Recipe</u>	<u>1</u>	<u>2A</u>	<u>3</u>	<u>4A</u>	<u>5</u>	<u>6B</u>
<u>Optimum Cure Time At 300°F</u>	12	60	17	51	25	13
Goodyear-Healey Rebound, % (opt. cure + 15 min.)	67.8	11.40	65.7	11.75	46.0	49.1

AGED VULCANIZATE PROPERTIESAged 1 Day at 70°C

<u>Stress-Strain</u>						
Tensile Strength, psi	2010	825	1830	1200	1860	1470
Elongation, %	300	175	290	275	420	210
300% Modulus, psi	2010	--	--	--	1350	--
Shore A2 Hardness	64	64	66	63	73	67

AGED VULCANIZATE PROPERTIESAged 3 Days at 70°C

<u>Stress-Strain</u>						
Tensile Strength, psi	1980	1000	1890	1245	2010	1880
Elongation, %	290	200	270	260	420	260
Modulus, psi	--	--	--	--	1460	--
Shore A2 Hardness	64	65	66	63	74	72

AGED VULCANIZATE PROPERTIESAged 5 Days at 70°C

<u>Stress-Strain</u>						
Tensile Strength, psi	1920	695	1330	1185	1890	1730
Elongation, %	280	120	200	230	400	240
300% Modulus, psi	--	--	--	--	1500	--
Shore A2 Hardness	66	64	66	62	73	71

AGED VULCANIZATE PROPERTIESAged 7 Days at 70°C

<u>Stress-Strain</u>						
Tensile Strength, psi	1520	950	1740	1150	1820	1990
Elongation, %	200	160	240	220	380	260
Shore A2 Hardness	67	65	68	60	73	73

TABLE XXXVI CONTD.

<u>Recipe</u>	<u>1</u>	<u>2A</u>	<u>3</u>	<u>4A</u>	<u>5</u>	<u>6B</u>
Optimum Cure Time @300°F, min.	12	60	17	51	25	13
Dynamic Ozone Cracking						
100°F, 50 pphm						
4 hrs.	NC*	NC	NC	NC	NC	NC
24 hrs.	FGC**	FGC	FGC	FGC	FGC	FGC
48 hrs.	FGC	FGC	FGC	FGC	FGC	FGC
72 hrs.	FGC	FGC	FGC	FGC	FGC	FGC

* No Cracking

**Fine General Cracking

IMMERSION PROPERTIES

Immersed 1 day in ASTM #3 Oil at 158°F

Weight Change, %	76.8	46.47	74.4	53.15	7.1	7.5
Volume Change, %	90.5	55.83	85.6	64.09	7.8	8.3

Stress-Strain Properties

Tensile Strength, psi	680	600	790	690	1890	1480
Elongation, %	120	120	150	140	490	250
100% Modulus, psi	--	--	--	--	1120	--
Shore A2 Hardness	45	43	45	47	64	65

Immersed 3 days in ASTM #3 Oil at 158°F

Weight Change, %	92.1	61.36	91.6	64.84	10.3	10.5
Volume Change, %	109.1	74.03	106.1	78.66	11.6	11.9

Stress-Strain Properties

Tensile Strength, psi	710	550	570	675	1800	1580
Elongation, %	120	130	110	140	410	250
300% Modulus, psi	--	--	--	--	1340	--
Shore A2 Hardness	46	42	46	44	65	64

Immersed 5 days in ASTM #3 Oil at 158°F

Weight Change, %	93.6	64.3	92.3	65.2	11.0	14.8
Volume Change, %	111.3	77.4	107.5	78.8	12.5	16.7

Stress-Strain Properties

Tensile Strength, psi	750	560	58	710	1660	1090
Elongation, %	130	120	110	130	370	190
300% Modulus, psi	--	--	--	--	1380	--
Shore A2 Hardness	45	40	48	44	62	65

TABLE XXXVI CONT.

<u>Recipe</u>	<u>1</u>	<u>2A</u>	<u>3</u>	<u>4A</u>	<u>5</u>	<u>6B</u>
<u>IMMERSION PROPERTIES CON'T.</u>						
Immersed 7 days in ASTM #3 Oil at 158°F						
Weight Change, %	96.0	61.49	96.9	69.32	13.3	12.5
Volume Change, %	113.6	74.52	112.4	84.03	15.3	14.1
<u>Stress-Strain Properties</u>						
Tensile Strength, psi	620	490	990	600	1700	1250
Elongation, %	110	120	150	120	380	180
300% Modulus, psi	--	--	--	--	1410	--
Shore A2 Hardness	42	39	44	43	62	65
Immersed 1 day in Water at 158°F						
Weight Change, %	8.8	18.25	7.3	16.70	18.6	14.3
Volume Change, %	9.5	19.20	7.7	17.66	20.3	15.5
<u>Stress-Strain Properties</u>						
Tensile Strength, psi	920	300	580	450	940	760
Elongation, %	300	300	280	300	480	300
300% Modulus, psi	920	300	--	450	440	760
Shore A2 Hardness	60	35	55	40	47	54
Immersed 3 days in Water at 158°F						
Weight Change, %	12.5	37.16	11.0	28.23	27.6	22.8
Volume Change, %	13.44	40.79	11.7	31.03	30.3	24.8
<u>Stress-Strain Properties</u>						
Tensile Strength, psi	890	290	540	390	800	580
Elongation, %	300	300	240	250	440	210
300% Modulus, psi	890	--	--	--	490	--
Shore A2 Hardness	57	30	55	32	47	52
Immersed 5 days in Water at 158°F						
Weight Change, %	15.3	45.7	13.5	38.7	28.4	26.14
Volume Change, %	16.6	49.9	14.3	42.5	31.1	27.2
<u>Stress-Strain Properties</u>						
Tensile Strength, psi	920	280	580	390	790	770
Elongation, %	300	260	240	270	420	290
300% Modulus, psi	920	--	--	--	490	--
Shore A2 Hardness	55	25	53	28	45	53

TABLE XXXVI CONTD.

<u>Recipe</u>	<u>1</u>	<u>2A</u>	<u>3</u>	<u>4A</u>	<u>5</u>	<u>6B</u>
<u>IMMERSION PROPERTIES CON'T.</u>						
Immersed 7 days in Water at 158°F						
Weight Change, %	16.8	55.93	13.4	45.48	30.9	31.8
Volume Change, %	17.9	61.82	13.9	50.26	34.0	34.9
<u>Stress-Strain Properties</u>						
Tensile Strength, psi	840	275	570	390	580	720
Elongation, %	290	300	210	240	360	270
300% Modulus, psi	--	275	--	--	460	--
Shore A2 Hardness	54	28	51	32	44	51

TABLE XXXVII
SBR STOCKS
COMPARISON OF NON-BLACK FILLERS WITH STARCH

	<u>HiSil</u>	<u>Silene D</u>	<u>Dixie Clay</u>	<u>Starch</u>
Ameripol 1708	137.50	137.50	137.50	--
Lot B2	--	--	--	220.00
Zinc Oxide	5.00	5.00	5.00	5.00
Stearic Acid	1.00	1.00	1.00	2.00
HiSil	75.00	--	--	--
Silene D	--	75.00	--	--
Dixie Clay	--	--	75.00	--
Flexol 460	5.00	5.00	5.00	--
Picco 25	5.00	5.00	5.00	--
PBNA	--	--	--	1.25
Altax	1.50	1.50	1.50	--
Methyl Tuads	.50	.50	.50	--
Ethylac	--	--	--	1.25
Sulfur	1.50	1.50	1.50	2.00
Total	232.20	232.20	232.20	231.50
Compound Mooney, ML-4	--	--	--	52

Physical Properties @Opt. Cure

Tensile Strength, psi	1840	1375	560	1270
Modulus, psi (300%)	725	700	340	1140
Elongation, %	610	500	450	370
Shore A2 Hardness	65	50	40	59

TABLE XXXVIII
NITRILE STOCKS
COMPARISON OF NON-BLACK FILLERS WITH STARCH

	<u>HiSil</u>	<u>Silene D</u>	<u>Dixie Clay</u>	<u>Starch</u>
Hycar 1032	100.00	100.00	100.00	--
Lot H	--	--	--	131.23
Zinc Oxide	5.00	5.00	5.00	5.00
Stearic Acid	1.00	1.00	1.00	2.00
HiSil	75.00	--	--	--
Silene D	--	75.00	--	--
Dixie Clay	--	--	75.00	--
Flexol 460	5.00	5.00	5.00	--
Picco 25	5.00	5.00	5.00	--
PBNA	--	--	--	1.25
Altax	1.50	1.50	1.50	--
Methyl Tuads	.50	.50	.50	--
Bismate	--	--	--	.625
Sulfur	1.50	1.50	1.50	2.00
Total	193.50	193.50	193.50	142.13
Compound Mooney (ML-4)	--	--	--	76

Physical Properties @Opt. Cure

Tensile Strength, psi	3390	1470	1710	2160
Modulus, 300% psi	1260	1090	1200	1900
Elongation, %	570	410	640	340
Shore A2 Hardness	82	75	62	70

TABLE XXXIX
EVALUATION OF STARCH MB/1833 BLENDS

	A*	B	C
Ameripol 1833-G1	245.00	183.75	122.50
Lot C	--	32.81	65.62
Zinc Oxide	3.00	3.00	3.00
Stearic Acid	2.00	2.00	2.00
Santocure	1.40	1.40	1.40
Unads	.20	.20	.20
Sulfur	2.00	2.00	2.00
Total	253.60	225.16	196.72

Monsanto Rheometer

3° arc, 3 cpm, 280°F

Maximum Torque	52	54	56
Minimum Torque	5.5	3.5	4.5
Scorch Time (t ₂), Min.	20	26	22
Optimum Cure (t ₉₀), Min.	38	45	41

UNAGED VULCANIZATE PROPERTIES

<u>Stress-Strain</u>	<u>Min. Cured @280°F</u>			
Tensile Strength, psi	30	2600	2590	2700
	40	2700	2700	2250
	60	2550	2425	2400
Elongation, %	30	610	630	570
	40	550	600	470
	60	510	510	470
300% Modulus, psi	30	1100	1000	1200
	40	1250	1125	1240
	60	1350	1220	1310
Shore A2 Hardness	30	60	57	60
	40	60	58	60
	60	61	60	60

* Date from Previous BFGCC Report

Lot C - 100 SBR, 30 phr starch, 1.23 RF

Ameripol 183361 - 100 SBR, 62.5 HA Oil, 82.5 HAF H.S.

TABLE XXXIX CONTD.

<u>Recipe</u>	<u>A</u>	<u>B</u>	<u>C</u>
Goodrich Flex (.175" stroke, 55 lbs. load) (Opt. cure + 15 min.)			
Initial Static Compression	.262	.252	.210
Initial Dynamic Compression	.183	.161	.123
Delta T, °F	54	36	34
Permanent Set, %	10.5	6.8	6.4
DeMattia Flex Flexures to 0.6" Crack growth, (RT) (Opt. cure + 4 min.)	--	20,106	27,934
Pico Abrasion Index (Opt. cure + 8 min.)	91	92	92
Garvey Die Data Speed 50 rpm, Heat 220°F Barrel 100°F			
Inches/min.	--	82.4	66.0
Grams/min.	--	158.0	148.0
Grams/inch	--	1.92	2.24
Rating			
Contour	--	4	3.5
Edge	--	4	4
Surface	--	4	4
Corners	--	4	4
Total	--	16	15.5



Rubber Products Molding Trials

Application compounds were developed for factory molding trials. Compounds RT-1, RT-2 and RT-3 (Table XXXX) were developed as retread compounds. Ameripol 1808 (RT-1) was selected as being typical of the SBR black masterbatches used in the tread rubber industry. Using 1808 as the control masterbatch, 25 and 50% starch masterbatch was substituted for it in a typical recipe. The recipes and test data are shown in the table. The resulting processing and physical properties were typical of retread compounds.

After having developed the compounds, we mixed approximately 10 to 12 lbs. of each and stripped it from the mill for use in an Orbitread machine. The stripped stock was taken to the B.F. Goodrich, Brookpark Retread Shop for application on buffed tires. Ten, new 8.25 X 14 nylon tires were obtained for use in this program. These tires were buffed and cemented similar to the regular retreading procedures.

The stock was extruded through an Orbitread machine onto the casings. The 50% starch/SBR masterbatch was extremely dry and obviously needed a tackifier to improve adhesion to the carcass. Satisfactory tires were built and cured. Two have been mounted on a local for wear evaluations.

The same stocks used in the retread trials were tested for cure characteristics at 320°F. These data indicated that cure times were reasonable (15 minutes) for molded products. Several cures of each stock were made in oil seal and O ring molds in order to determine the molding characteristics. The results indicate that the blends of Ameripol 1808 and a starch masterbatch can be used for many molded products. The physical properties would be adequate for a variety of applications. In addition, these compounds could be adjusted to give a faster cure or other improved physical properties.

Three Hycar 1032/starch masterbatch compounds were developed to meet ASTM D2000 BG specifications, Table XXXXI. Actually, the compounds pass the requirements for a 2BG615 specification except for water immersion. These compounds could be used in applications calling for this specification if the water specification could be varied.

Six to eight pounds of each stock was mixed along with a Hycar/carbon black recipe selected from the literature. The stocks were taken to the Enduro Rubber Company in Ravenna, Ohio, and molded into a variety of finished products. Various mold designs were selected to evaluate the knitting, hot tear and flow characteristics of these stocks. In all cases, the Hycar 1032/starch stocks molded without any problems. Some of the molds had extremely intricate undercuts which required exceptionally good flow and hot tear.

The molds were selected because of their intricate designs and the fact that they were readily available. Most of the products would not require the oil resistance and aging characteristics of the Hycar 1032/starch compounds. However, these evaluations indicate that the Hycar 1032/starch stocks could be used to mold most products requiring the special oil resistant properties.

One stock ST-3 was taken to the Lewis Division of the McDowell Wellman Industries for injection molding trials. A 16 cavity brake cup mold was used in this evaluation along with the Lewis ram injection molding machine. The stock molded well indicating that the SBR/starch masterbatch could be used for injection molding applications.

Based on the molding trials and physical test data (except water resistance) the Hycar/starch masterbatches could be used for the many molded products calling for the 2BG615 specifications. These applications would include products such as diaphragms, gaskets, O Rings, packings, seals, bushings, etc.

The composition of the Hycar and SBR starch masterbatches and the Ameripol 1808 masterbatch are shown in Table XXXXII.

TABLE XXXX
Evaluation of Starch MB/1808 Blends

<u>Ingredients</u>	<u>RT-1</u>	<u>RT-2</u>	<u>RT-3</u>
Ameripol 1808	225.00	168.75	112.50
Lot B-2	--	55.00	110.00
Zinc Oxide	3.00	3.00	3.00
Stearic Acid	2.00	2.00	2.00
Santocure	1.40	1.40	1.40
Unads	.20	.20	.20
Sulfur	2.00	2.00	2.00
Total	233.60	232.10	231.10

Compound Mooney, ML-4, @212°F	39	37	45
-------------------------------	----	----	----

Monsanto Rheometer

3° arc, 3 cpm, 280°F

Maximum Torque	56	54.5	53
Minimum Torque	5.5	5	4
Scorch Time, t ₂ min.	22	22	21.5
Optimum Cure, t ₂ min.	34	38	41.5

Monsanto Rheometer

3° arc, 3 cpm, 320°F

Maximum Torque	52	50	48
Minimum Torque	5	4.5	4
Scorch Time, t ₂ , Min.	7.5	7.5	8
Optimum Cure, t ₉₀ , Min.	12	13	13

UNAGED VULCANIZATE PROPERTIES

Min. Cured

Stress-Strain

@280°F

Tensile Strength, psi	30	2950	2350	2050
	40	2800	2300	2100
	60	2850	2300	2100
Elongation, %	30	500	520	470
	40	470	480	470
	60	460	430	460
300% Modulus, psi	30	1500	1350	1150
	40	1550	1450	1250
	60	1625	1600	1300
Shore A2 Hardness	30	60	58	58
	40	60	58	58
	60	61	59	58

TABLE XXXX CONTD.

UNAGED VULCANIZATE PROPERTIES CONTD.

<u>Stress-Strain</u>	<u>Min. Cured</u> <u>@320°F</u>			
Tensile Strength, psi	10	2650	2175	1950
	15	2750	2300	2000
	20	2700	2250	2050
Elongation, %	10	450	480	450
	15	430	500	440
	20	440	450	420
300% Modulus	10	1100	1150	1100
	15	1350	1200	1150
	20	1425	1300	1200
Shore A2 Hardness, psi	10	58	58	57
	15	59	58	58
	20	59	58	57

TABLE XXXXI
NITRILE STARCH MASTERBATCH EVALUATION

Ingredients	ST-1	ST-2	ST-3
Lot H-2	131.23	131.23	131.23
Zinc Oxide	5.00	5.00	5.00
TP 90B	7.50	15.00	--
PBNA	1.50	1.50	1.50
Altax	1.50	1.50	1.50
Stearic Acid	2.00	2.00	2.00
Methyl Tuads	.25	.25	.25
N770	--	15.00	--
Sulfur	1.50	1.50	1.50

Compound Mooney, ML-4 @212°F	39	37	55
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Monsanto Rheometer

3° arc, 3 cpm, 320°F			
Maximum Torque	48	37	51.5
Minimum Torque	2.5	2.5	3
Scorch Time, t ₂ Min.	5	5	5.5
Optimum Cure, t ₂ Min.	6.5	8	8

UNAGED VULCANIZATE PROPERTIES

Stress-Strain	Min. Cured @320°F				Spec.
Tensile Strength, psi	10	1700	1600	1650	1500 min.
	15	1650	1550	1650	
	20	1600	1525	1625	
Elongation, %	10	430	420	410	300 min.
	15	460	440	340	
	20	420	410	360	
300% Modulus, psi	10	800	925	1200	
	15	775	875	1125	
	20	800	950	1100	
Shore A2 Hardness	10	60	57	61	60 ₊₅
	15	58	57	63	
	20	58	56	62	

Heat Aged ASTM D573 70 hrs. @100°C

Tensile Strength, psi	10	-4	-8	+8	±30%
(change)					
Elongation, %	10	0	-32	-12	-50%
(change)					
Hardness, pts	10	+2	+10	+8	±15 pts.

TABLE XXXXI CONTD.

Oil Immersion ASTM D471 No. 1 Oil, 70 hrs. @212°F

	<u>ST-1</u>	<u>ST-2</u>	<u>ST-3</u>	<u>Spec.</u>
	<u>-4</u>	<u>+4</u>	<u>+15</u>	<u>-25</u>
Tensile Strength % Change				
Elongation % Change	-20	-22	-0	-45
Shore A2 Hardness % Change	0	+6	-1	-5 to +10
Volume Change %	-6.2	-8.8	-.5	-10 to +5

Oil Immersion ASTM D471 No. 3 Oil, 70 hrs. @212°F

Tensile Strength % Change	-30	-29	-12	-45
Elongation % Change	-23	-20	-18	-45
Volume Change %	11	16	16	0 to +25

Fluid Immersion ASTM D471 Fuel A, 70 hrs. @73°F

Tensile Strength % Change	-24	-28	+5	-25
Elongation % Change	-5	-12	0	-25
Shore A2 Hardness pts. change	-3	-3	0	+10
Volume Change %	+2	+9	+3	-5 to +10

TABLE XXXXI CONTD.

<u>Recipe</u>	<u>ST-1</u>	<u>ST-2</u>	<u>ST-3</u>	<u>Spec.</u>
<u>Fluid Immersion ASTM D471 Fuel B</u>				
Tensile Strength % Change	-45	-42	-25	-60
Elongation % Change	-40	-33	-31	-60
Shore A2 Hardness % Change	-13	-9	-14	0 to -30
Volume Change, %	+29	+35	+36	0 to +40
<u>Compression Set, ASTM D395, Solid, Max. percent, 22 hrs. @100°C</u>				
Compression Set, %	33	32	29	50
<u>Water Immersion ASTM C471, 70 hrs. @212°F</u>				
Shore A2 Hardness, % Change	-17	-15	-14	+10
Volume Change, %	38	25	38	+15

TABLE XXXXII
Composition of Masterbatches PHR

	<u>SBR</u>	<u>Hycar</u>	<u>SBR</u>
Starch Xanthide	70	30	--
Sunthene 380 Oil	50	--	--
Polymer type	SBR 1708	Hycar 1032	SBR 1712
	100	100	100
HA Oil	--	--	50
HAF N330 Carbon Black	--	--	75
Paraformaldehyde & Resorcinal	--	1.23	--

Project Assessment

The assessment of this project is divided into two sections. These are roughly speaking: (1) The recommendations for specific future work, and (2) The long term view.

There are several critical areas in the design which must be investigated further. These are: (1) Alternate oxidants to avoid the problems associated with nitrogen oxide gas evolution, (2) Filtering or dewatering the crumb, and (3) Drying the filtered crumb evenly to 10-20% moisture. While these are all technical problems, their primary significance is economic. If a less hazardous oxidant can be used, extra ventilation and scrubbing may not be required. The filtering process must be improved to reduce the excessive water load on the dryer. Usually it is cheaper to reduce the water level as much as possible mechanically before the evaporative drying step. Because of the high inlet water level, excessive drying times were experienced. Furthermore, the drying tended to be uneven, that is, there were very dry spots and very wet spots. The crumb becomes sticky during a portion of the drying cycle. At this point the crumbs agglomerate and adhere to the dryer apron or tray. After this the crumbs tend to crust over giving an uneven drying rate. The extrusion dryer feed should have a uniform moisture level. A non-homogeneous feed to the Anderson Expander is suspected as a possible reason for its somewhat poorer performance compared with the laboratory Brabender extruder. A uniform feed should improve the starch dispersion or particle size properties.

In addition there are several less critical areas which could bear further investigation: (1) continuous xanthation, (2) coagulation mixer, (3) serum recycle process, (4) extrusion processing equipment and conditions, and (5) packaging. These items have generally been studied sometime before but have not necessarily been optimized. Continuous xanthation with very little hold-up time was assumed in the design. The USDA has a continuous xanthation process but the immediate blending with latex and coagulation has not been tested. The USDA speculates xanthation may require some time for an efficient reaction. Packaging should be studied since several forms might be practical. Also, the need for vapor proof covering must be investigated if water absorption becomes a problem.

Historically no filler or reinforcing agent for rubber has been commercialized initially as a non-dry or "wet" mixed masterbatch. The only commercially available non-dry mixed masterbatches are oil, oil/black, black, and styrene resin masterbatches. Each of these were initially evaluated using dry mixes. Also, dry mixing continues except for the high volume items. Thus, the black masterbatches that are commercially available from a synthetic rubber producer are made for high volume uses, such as retreads, or are useful for many smaller volume applications. The industry has taken a number of years to evolve to its present position. Even where black masterbatches are used eventually, the initial compounding studies are often based on dry mixes. The masterbatches are generally produced to fill a customer or industry-wide demand either by direct request or by testing the market with different compositions. While most SBR producers make a variety of black masterbatches, no other rubber is sold as black masterbatch using a "wet" mix process except one supplier of cis-polybutadiene.

Given this situation it is very difficult to introduce a material in a masterbatch form. The polymer may be wrong, the composition may be wrong, the modifications may be wrong, any number of things make this route difficult. A further complication to the masterbatch route is the commitment needed by a rubber producer. General purpose elastomers are inexpensive in large part because of the volume produced. To maintain these favorable economics, any subclass of the product, such as masterbatches, must also be produced in volume or incur an economic penalty. This, of course, is in the opposite direction needed for marketing where a low initial volume is needed to test and develop the market. This phase is generally handled with pilot plant operations. Undoubtedly, the starch masterbatch would have to be produced on a pilot plant scale several years. During this time extensive background compounding and physical testing data would be gathered to interest potential customers. Because starch would be competing with existing rubber reinforcing agents, the pilot plant operation would inevitably be an economic drain. With a unique, new product it may be possible to sell the limited quantities of pilot plant material at a high enough price to recover the pilot plant expense. This would not be the case with starch/SBR or NBR masterbatches. At this time, the risk involved with such an investment is not justified by the potential return. While the evaluations to date have been far from exhaustive, no unique, desirable property of significance has been found which would justify the investment for a semi-commercial pilot plant operation plus a full scale production facility. Of course, in this day of raw material shortages starch masterbatches can not be ruled out completely as a potential substitute or partial substitute for carbon black or other reinforcing fillers. Further work on starch masterbatches could be considered as insurance against carbon black supply shortages.

